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# **Pulsed Laser Annealing of Carbon**

A Dissertation in

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by

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## ABSTRACT

This dissertation investigates laser heating of carbon materials. The carbon industry has been annealing carbon via traditional furnace heating since at least 1800, when Sir Humphry Davy produced an electric arc with carbon electrodes made from carbonized wood. Much knowledge has been accumulated about carbon since then and carbon materials have become instrumental both scientifically and technologically. However, to this day the kinetics of annealing are not known due to the slow heating and cooling rates of furnaces. Additionally, consensus has yet to be reached on the cause of nongraphitizability.

Annealing trajectories with respect to time at temperature are observed from a commercial carbon black (R250), model graphitizable carbon (anthracene coke) and a model nongraphitizable carbon (sucrose char) via rapid laser heating. Materials were heated with 1064 nm and 10.6 µm laser radiation from a Q-switched Nd:YAG laser and a continuous wave CO<sub>2</sub> laser, respectively. A pulse generator was used reduce the CO<sub>2</sub> laser pulse width and provide high temporal control. Time-temperature-histories with nanosecond temporal resolution and temperature reproducibility within tens of degrees Celsius were determined by spectrally resolving the laser induced incandescence signal and applying multiwavelength pyrometry. The Nd:YAG laser fluences include: 25, 50, 100, 200, 300, and 550 mJ/cm<sup>2</sup>. The maximum observed temperature ranged from 2,400 °C to the  $C_2$ sublimation temperature of 4,180 °C. The CO<sub>2</sub> laser was used to collect a series of isothermal (1,200 and 2,600 °C) heat treatments versus time (100 milliseconds to 30 seconds). Laser heated samples are compared to furnace annealing at 1,200 and 2,600 °C for 1 hour. The material transformation trajectory of Nd:YAG laser heated carbon is different than traditional furnace heating. The traditional furnace annealing pathway is followed for CO<sub>2</sub> laser heating as based upon equivalent end structures. The nanostructure of sucrose char after 5 seconds of isothermal annealing at 2,600 °C is comprised almost entirely of quasi-spherical closed shell particles that are free of sp<sup>3</sup> and oxygen content. With additional time at temperature the particles unravel and propagative particle opening occurs throughout the material. The irregular pore structure found in the end product is a result of particle unraveling. The structures found in heat treated sucrose char believed to contain odd membered rings are not manufactured during the annealing process due to impinging growth of stacks. Thus, odd membered rings are likely present in the starting non-graphitizable char.

Furnace annealing of cokes and chars produced from: oxygen containing compounds (polyfurfuryl alcohol and anthanthrone), from a five membered ring containing polyaromatic hydrocarbon (fluorene), and from sulfur containing decant oil and a blend of anthracene-dibenzothiophene were compared to furnace annealed anthracene coke and sucrose char. The majority of initial oxygen content evolved out during low temperature carbonization. The intermediate species formed after oxygen evolution dictated the resulting carbon skeleton and thus the graphitizability. Carbonization of anthanthrone resulted in a graphitizable coke. It is proposed that carbon monoxide loss from anthanthrone results in the formation of perylene. An obvious resemblance was observed in structure between heat treated sucrose and polyfurfuryl alcohol char as compared to heated treated char embedded with 5 membered rings via carbonization of fluorene. Thus, providing evidence that 5 membered rings are present in the virgin chars and are the cause of non-graphitizability.

The heteroatom sulfur effects carbon structure in a different way as compared to oxygen. Sulfur is thermally stable in carbon up to ~ 1,000 °C and thus plays little role in the initial low temperature (500 °C) carbonization. As such it imparts a relatively unobservable impact on nanostructure, but rather acts to cause micro-cracks upon rapid evolution in the form of H<sub>2</sub>S and CS<sub>2</sub>, upon subsequent heat treatment. Laboratory generated synthetic soot from benzene and benzene-thiophene were Nd:YAG laser and furnace annealed. Furnace annealing of sulfur doped synthetic soot results in cracks and rupturing due to the high pressures caused by explosive sulfur evolution at elevated temperature. Whereas Nd:YAG laser heating of the sulfur doped sample acted to induce curvature. The observed curvature is owed to annealing occurring simultaneously with sulfur evolution. The unset lamellae are strongly influenced by the defect formed upon sulfur evolution.

Coke and char samples were prepared via carbonization in sealed tubing reactors. The extent of mesophase development was assessed by measuring the materials optical anisotropy with a polarized light microscope. Physical and chemical transformations from annealing were measured with electron microscopy, energy dispersive X-ray spectroscopy, selected area electron diffraction, and electron energy loss spectroscopy. Virgin samples and traditional furnace annealed samples available in bulk were analyzed with X-ray diffraction.

The potential technological importance of laser annealing carbon is demonstrated as annealing can be performed continuously and rapidly. Examples of material processing and synthesis not possible via traditional furnace annealing are provided.

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## ACRONYMS

BSU	Basic Structural Unit
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
DBT	Dibenzothiophene
DO	Decant Oil
EDS	Energy Dispersive X-Ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
НТТ	Heat Treatment Temperature
HRTEM	High Resolution Transmission Electron Microscopy
ICCD	Intensified Charge Coupled Device
IR	Infrared
LASER	Light Amplification by Stimulated Emission of Radiation
РАН	Polycyclic Aromatic Hydrocarbon
PFA	Polyfurfuryl alcohol
PMT	Photomultiplier Tube
RF	Radio Frequency
SEM	Scanning Electron Microscopy
SSILD	Soot Source Identification by Laser Derivatization
TEM	Transmission Electron Microscopy
XRD	X-Ray Diffraction
YAG	Yttrium Aluminum Garnet

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## **Chapter 1**

## Introduction

#### **1.1 Introduction**

Thermal annealing of carbon is an age old process that has been occurring since at least the earliest conversion of carbon feedstocks to graphite in the Earth's crust and upper mantel. The carbon industry appears to have had its beginning in 1800, when Sir Humphry Davy produced an electric arc with carbon electrodes made from carbonized wood.<sup>1</sup> During the remainder of the 19<sup>th</sup> century, the carbon industry focused on improving the electrodes for arc lighting. In 1886, it was discovered that turbostratic carbons upon heat treatment at sufficiently high temperatures converted to graphite.<sup>1</sup> Heat treatment of carbon was further elucidated in 1950 by the seminal work of Franklin, who published X-Ray Diffraction (XRD) studies on heat treated carbons derived from carbonization of hydrocarbons and other organic carbon feedstocks. She showed that upon heat treatment up to 3,000 °C, the interplanar (002) spacing decreased to approximately 3.354 Å, the value of crystalline graphite.<sup>2,3</sup> Since then, heat treatment of carbon has been extensively studied with an emphasis on identifying structural transformation dependence upon Heat-Treatment-Temperature (HTT). Structural changes based on HTT have been extensively studied for carbon material formed via thermal decomposition (i.e. pyrolysis) of organic precursors.

A vast accumulation of knowledge has been gained regarding HTT studies. However, HTT studies are purely based on thermodynamics (i.e. temperature) and little attention has been directed towards annealing kinetics. In fact, most studies on structural changes during heat treatment only provide HTT and nothing is mentioned about time above temperature. Needless to say, measuring kinetics of solid-state reactions at temperatures above 2,000 °C are challenging experimentally. The experimental challenge is in the control of achieving short time durations at precise elevated temperatures. The ideal kinetic carbon annealing study would measure annealing extent in situ under isothermal heat treatment. Such measurements are technically feasible using in situ XRD. However, such measurements at elevated temperatures are plagued by the c-axis thermal expansion of carbon at graphitization heat treatment temperatures. The  $d_{002}$  spacing increases by nearly 10% when heated to 2,500 °C, whereas the decrease in spacing due to graphitization (measured at ambient temperature) is only about 2%. A more serious complication, one that likely cannot be accounted for, rendering in situ XRD measurements not useful for kinetic studies is that the c-axis thermal expansion coefficient is a function of carbon crystalline perfection (i.e. not easily removed as exact knowledge of structure and thermal expansion is required). With in situ kinetic measurements ruled out due to the unknown material properties at elevated temperatures, the next best kinetic study is an isothermal heat treatment versus time. The ideal heat treatment would bring the sample to temperature instantaneously, remain constant for a desired duration, and then instantaneously cool to ambient. Such a heating scheme is not possible but has been approximated by either direct resistive (Joule) heating and by rapid sample insertion into preheated graphitization furnaces. Joule heating may result in non-uniform temperature with challenging sample preparation and experimental configuration. Due to the configurational difficulty involved in Joule heating and sample retention, the rapid insertion technique has historically received more attention. Traditional furnace heating is limited to time scales no less than several minutes due to slow ramp rates. At this time scale the only material transformation that is rate restricted is the layer plane spacing reduction and the rates of this spacing reduction with respect to temperature are well known for these time scales (i.e. several minutes minimum).

Lasers can heat carbon materials to graphitization temperature within nanoseconds to milliseconds, depending on laser light source. On these extremely short time scales, the extent of material transformation is kinetically limited by time above temperature. Therefore, laser heating can be used to study the rates and trajectories of carbons during annealing. Short heating durations enable the annealing pathway of graphitizable and non-graphitizable carbons to be followed and contrasted. The exact nature of cross-links responsible for non-graphitizability are still unknown. Monitoring the materials trajectory with respect to time at temperature can provide insight into the nature and formation mechanism of cross-links found in heat treated non-graphitizable carbons.

### **1.2 Hypotheses**

1. Optical anisotropic regions as observed under a polarized light microscope are locked in place following the completion of mesophase development. Subsequent heat treatment will not result in increased optical texture sizes through long range material restructuring.

2. If non-graphitizing elements, believed to be odd membered rings, can be incorporated into the layer planes formed during mesophase, the optical anisotropy will be lost upon subsequent heat treatment. Thus, mesophase development in and of itself does not exclusively result in graphitizable carbons as is the current definition. The odd membered rings embedded in a coke formed through mesophase will induced curvature and become accentuated via lamellae growth upon subsequent heat treatment.

3. The non-graphitizability of chars formed from oxygen rich precursors is due to the formation of odd membered rings, predominantly pentagonal, upon the evolution of oxygen atoms during carbonization. Subsequent graphitization heat treatment of these materials results in a fullerenic-like nanostructure.

4. Laser annealing provides the energy required for graphitization and can be controlled in such a way that annealing either follows or deviates from traditional furnace annealing trajectories.

a) High energy density Nd:YAG laser annealing rapidly heats (nanoseconds) carbon to graphitization heat treatment temperature. All activation energies including: devolatilization, conversion of sp<sup>3</sup> hybridized carbon to sp<sup>2</sup> hybridized carbon, lamellae mobilization and growth, reorientation, de-wrinkling, and alignment (d-spacing), occur almost simultaneously. Whereas traditional furnace

annealing provides a much slower energy addition rate and thus traditional annealing steps are delayed based on heating rate and occur in a step wise fashion. Nd:YAG laser heating will alter annealing trajectory due to heating rate and insufficient time at elevated temperature.

b) Continuous wave  $CO_2$  laser annealing heats carbon to graphitization heat treatment temperature within a millisecond. Carbon annealing will follow the traditional furnace annealing pathway at this energy addition rate.

## 1.3 Goals

In addition to evaluating the above hypotheses, the goals of this work include:

- 1. To provide evidence that odd membered carbon rings are present in virgin chars derived from oxygen containing precursors and are the cause of their non-graphitizability.
- 2. To determine the rates of carbon transformations during annealing by rapid heating and cooling via pulsed laser annealing. Observe the annealing trajectories from a model graphitizable and non-graphitizable carbon at the earliest stages of the annealing process.
- 3. Demonstrate the ability of laser heating for the purpose of rapid annealing and material processing.
- 4. Synthesize novel materials only possible via laser annealing.

These goals serve to carry out an in depth study on fundamental carbon science and technology development. A focus is placed on determining the structure of cross-links that result in non-graphitizability. To resolve the detailed morphological and nanostructural changes, high resolution transmission electron microscopy (HRTEM) is used to examine the carbons before and after annealing. The term nanostructure is used here to refer to the graphene layer plane dimensions, their tortuosity and relative orientation as observed in the HRTEM images. The term fullerenic-like is used throughout this dissertation to refer to quasi-spherical nanoparticles and half spherical carbon nanotube endcap like structures that as a requirement of existence must contain odd membered carbon rings.

## **Chapter 2**

## **Literature Review**

This chapter provides a review of the pertinent carbon literature focused on annealing, kinetics of annealing, and graphitizability. The first topic introduced is that of carbonization. Carbonization encompasses the production of many forms of carbon and the discussion is limited to pyrolytic carbon, carbon black and soot, coke, and char. An extended discussion on mesophase is provided as mesophase development during carbonization is the key to graphitizability. Following carbonization, structural transformations based on heat-treatment-temperature (HTT) are reviewed. The limited kinetic studies are reviewed after introducing HTT (i.e. thermodynamics). Concepts used to explain the observed non-graphitizability of cross-linked carbons are presented in chorological order. Despite the wide use of laser processing in industry, laser annealing of carbon material remains uncommon. Lasers for the purpose of annealing carbon are briefly discussed.

### 2.1 Carbonization

The carbonization process is initiated by the formation of free radicals at temperatures above 400 °C. Free radicals rapidly react with other radials or molecules through an overall dehydrogenation and dealkylation process, with the possibility of rearrangements and fragmentation forming new molecular species.<sup>4</sup> Carbonization is a complex process involving the formation of solid carbonaceous material from organic precursors and has been defined by the International Union of Pure and Applied Chemistry (IUPAC)<sup>5</sup> as:

#### "Description:

CARBONIZATION is a process by which solid residues with increasing content of the element carbon are formed from organic material usually by pyrolysis in an inert atmosphere.

Notes:

As with all pyrolytic reactions, CARBONIZATION is a complex process in which many reactions take place concurrently such as dehydrogenation, condensation, hydrogen transfer and isomerization."

From the above general definition, it is seen that carbonization applies to all precursor phases: gas, liquid, and solid. Where carbonization of a gas phase carbon precursor like acetylene yields either a pyrolytic carbon or a colloidal carbon (e.g. carbon black). A pyrolytic carbon refers to carbon deposited on a substrate by carbonization of a gaseous precursor (i.e. chemical vapor deposition (CVD)). Colloidal carbon is not deposited onto a substrate via CVD, but rather formed as an aerosol. Carbonization of liquid and solid organic precursors leads to the production of two distinct material classes: cokes and chars.

### 2.1.1 Pyrolytic Carbon

Pyrolytic carbons are by definition, carbon material deposited from gaseous hydrocarbons on suitable underlying substrates (carbon material, metals, and ceramics) via CVD.<sup>5</sup> Simply stated, pyrolytic carbon is solid carbon deposited onto a heated surface via thermal cracking of gaseous hydrocarbons. The term pyrocarbon was introduced as a trademark and is synonymous with pyrolytic carbon. Pyrolytic carbon structure depends upon reaction temperature, pressure, gas composition, substrate surface area and composition.<sup>6</sup> As hydrocarbons are fed into a furnace, colloidal carbon begins to form as an aerosol. Pyrolytic carbon forms on the underlying support. Colloidal carbon, depending on reaction conditions tends to deposit with the pyrolytic carbon, disturbing the structure.<sup>7</sup> Thus, these two forms of carbon are essentially competing with one another and in order to avoid colloidal carbon formation, temperature or pressure needs to be lowered.<sup>8</sup> When colloidal carbon formation and subsequent deposition of colloidal carbon is limited, the pyrolytic carbon structure is that of the so called "rough laminar" type. Rough laminar pyrolytic carbons appear as large cones covering the whole thickness of the deposit as represented by the cartoon illustration in Figure 2-1.<sup>7</sup>



Figure 2-1. Cartoon illustration of a rough laminar pyrolytic carbon.<sup>7</sup>

Poly-nucleated or granular pyrolytic carbons occur with increasing colloidal carbon deposition as illustrated by the cartoon image in Figure 2-2.



Figure 2-2. Cartoon illustration of granular pyrolytic carbon.<sup>7</sup>

Formation conditions (precursor species, pressure, temperature, and flow rate or residence time) and resulting properties of pyrolytic carbons have extensively been studied. The main characterization technique historically applied to pyrolytic carbon has been reflected polarized light microscopy. The optical texture of polished transverse sections under crosspolarizers is used to assign an optical texture. Following the work of Bokros<sup>9</sup>, authors agreed to distinguish between three main optical textures: laminar, granular, and isotropic. At lower temperatures and short residence times, smooth laminar pyrolytic carbons are observed and characterized by low reflectance. Longer residence times produce the rough laminar pyrolytic carbon characterized by high reflectance and optical rotary power (i.e. crystalline material with optical properties dependent upon directionality). Laminar pyrolytic carbons are crystalline and are readily graphitized upon subsequent heat treatment.<sup>7</sup> The granular texture is observed with increasing temperature as a result of colloidal carbon deposition perturbing the laminar pyrolytic carbon. At high temperatures an isotropic pyrolytic carbon is deposited and light is fully extinguished under crosspolarization regardless of stage rotation upon observation. This material is termed isotropic pyrolytic carbon as it lacks any anisotropy in its optical texture as observed by polarized light microscopy.

### 2.1.2 Colloidal Carbon - Carbon Black and Soot

#### 2.1.2.1 Carbon Black and Soot Formation

Carbonization of gaseous carbon precursors in aerosol leads to the formation of colloidal carbon. Colloidal carbon produced in industry is termed carbon black. Where anthropogenic soot is a carbonaceous material formed from the incomplete combustion of hydrocarbon fuels. Soot is an unwanted byproduct of combustion and carbon black is a manufactured product. The annual carbon black demand in the United States is 1.6 million metric tons.<sup>10</sup> The majority of this carbon black is used as a reinforcing agent in rubber with automotive tires accounting for 70% of total carbon black demand.<sup>10</sup> Another 20% is used in non-tire rubber application and non-rubber use such as paint, plastic, paper, ink, and ceramics make up the remaining 10% of the total carbon black demand. Over 95% of all carbon black is produced by the furnace black process.<sup>10</sup> Soot and carbon black are structurally very similar and are believed to follow the same general formation pathway.

Soot is a complex aerosol formed during incomplete combustion. The structure of the resulting soot is highly dependent upon the formation conditions, temperature, soot precursor molecular species available for soot growth and inception, pressure of the combustion process, and resonance time.<sup>11–14</sup> The aggregates of soot and carbon black are made up of several tens of pseudo-spherical individual primary particles. The primary particle size and the total aggregate size is dependent on many factors such as fuel, flame, engine, injector types, and operating conditions. Typical primary particle diameters range between roughly 10 nm up to a few hundred nm and aggregates have complex fractal geometries as shown in the transmission electron micrograph in Figure 2-3A.



Figure 2-3. Transmission electron micrographs of a commercial carbon black aggregate (A) and primary particle (B). (Source - Author).

As modern combustion engines continue to advance, the flame geometry and structure increases in complexity. Soot modeling has received a lot of attention over the past several decades and reasonable agreement has been found for many of the flames investigated.<sup>15</sup> The consensus in the field is that soot follows the hydrogen-abstraction-acetylene-addition (HACA) mechanism, pioneered by Frenklach and coworkers.<sup>16–18</sup> The HACA mechanism is believed to capture the essence of the sooting process. This mechanism involves a repetitive sequence of two principal reaction steps, the abstraction of a hydrogen atom from the reacting hydrocarbon by another hydrogen atom followed by the addition of an acetylene molecule to the radical site formed in the previous H-abstraction step. The HACA mechanism well describes the surface growth mechanism of soot and surface growth is responsible for the majority of soot mass.<sup>15</sup> The particle inception or nucleation is believed to occur around Poly-Aromatic Hydrocarbons (PAHs) via physical condensation. Soot inception is followed by growth via the HACA mechanism and via small aromatic molecules either fuel borne or built up from smaller molecular species. Followed by the physical process of primary particle aggregation. As growth continues to

occur during and after aggregation, the primary particles become both physically and chemically joined together as layers of carbon form over the perimeter and thus describing primary particles in an aggregate as point contacting spheres is an over simplification. Figure 2-4 schematically illustrates the process of soot inception, growth, aggregation, and oxidation steps, taken from the work of Bockhorn.<sup>12</sup>



Figure 2-4. Soot nucleation-growth-aggregation-oxidation pathway.<sup>12</sup>

Prior to the now celebrated HACA mechanism, there was disagreement regarding soot formation. Following their discovery of the buckminsterfullerene in 1985, Smalley et al. thought that soot formation and growth could be explained based on a fullerene like development.<sup>19,20</sup> The C<sub>60</sub> fullerene that they discovered by laser vaporization of graphite was believed to form from a graphene sheet that closed into a spheroidal shell at the high temperature. The reason for such transformation from flat to spherical was accredited to the stability increase of such a structure by the elimination of reactive edges.<sup>19,20</sup> To form a sphere or a soccer ball from a single layer of 60 carbon atoms, twelve five membered rings spaced equally from one another by six membered rings must be formed. Smalley et al. became interested in soot formation because soot primary particles like fullerenes are

spherical and the mechanism of soot inception was not well known. They postulated based on the observation of  $C_{60}$  and larger spheroidal carbon shells that the sphericity of soot is because carbon prefers spherical shells when faced with the necessity of satisfying the valence requirement.<sup>20</sup> Of course, this assumes the absence of other local atoms available for bonding and soot inception in flames occurs in regions rich in hydrogen. Smalley et al. explain carbon shell formation in flame by the fact that dehydrogenation is favored at flame temperature and thus local hydrogen does not bond to the carbon material and carbon shell formation is prefered.<sup>20</sup> They provided the icosahedral growth mechanism based on the pentagon-road model that was used for fullerene to explain soot inception and growth. The PAHs present in high concentrations in flames must form five membered rings (pentagons) to induce the curvature necessary for a spheroidal structure to form. The original model assumes successive shell formation forming an onion-like particle as shown in Figure 2-5.



Figure 2-5. Soot inception via the icosahedral model.<sup>20</sup>

Kroto and McKay refined the icosahedral model in favor of the quasi-icosahedral spiral shell model.<sup>21</sup> In the refined model, a quasi-single crystal particle of concentric spiral-shells are formed.<sup>21</sup> In this revised model, the initial fullerene fails to close and curls around itself forming a structure analogous to a nautilus shell. The proposed mechanism is shown in Figure 2-6.



Figure 2-6. Mechanism of the quasi-icosahedral spiral shell model.<sup>21</sup>

The quasi-icosahedral begins with the five membered ring containing PAH corannulene as displayed in Figure 2-6a. Continued condensation of corannulene leads to fullerene (b), however the fullerene fails to terminate in (c) and thus leads to the nautilus shell (d).

The concept of soot growth and inception as proposed by Kroto et al. was not accepted by the combustion community. Both Frenklach<sup>22</sup> and Ebert<sup>23</sup> provided strong denunciation. The argument made against the spiral shell model can be summarized into the following points:

- The transformation from planar to curved PAH would rate limit the growth of the fullerene shell due to the lower thermodynamic stability of bent molecules compared to planar molecules.
- Hydrogen to carbon ratios are typically between 0.1-0.3 for mature soot and the theoretical spiral shell model would be orders of magnitude lower.
- If soot was a spiral shell that contained appreciable five membered rings the (100) and (110) X-ray diffraction peaks would not match the planar benzenoid network values of 2.4 and 1.42 Å as has been demonstrated since the late 1930's.

Moreover, soot is not icospiral nor does it nucleate from  $C_{60}$ .<sup>24</sup> Ebert said, "suggesting that soot is formed from  $C_{60}$  because  $C_{60}$  is formed in flame is like saying graphite is formed from  $C_{60}$  because  $C_{60}$  is formed from arc discharge and laser vaporization of graphite."<sup>23</sup> Of course  $C_{60}$  is known to form in flames, albeit in very minute quantities.

Prior to the interesting few year period (1986-1990) with the back and forth about fullerene nucleated soot and the resulting single crystal spiral shell soot, several researchers proposed that soot and carbon black were formed through a liquid crystal phase or mesophase.<sup>25–27</sup> The logic again appears to be based on the spherical geometry of primary soot particles and the concentric arrangement of layered lamellae. The carbon lamellae found along the periphery of carbon black and soot primary particles lie approximately parallel to the surface and become more disordered towards the center of the particle, see Figure 2-3B. Further rationale for mesophase development is that carbon black is often produced from the same petroleum pitch that is used to make needle coke, a material known to develop mesophase upon carbonization. Figure 2-7 provides a schematic representation of a carbon black primary particle and a typical carbonaceous mesophase sphere. The carbon lamellae found in mesophase spheres formed during the production of cokes are not parallel to the surface (i.e. concentric), but are parallel to the equatorial planes and thus perpendicular to the surface. Marsh<sup>26</sup> suggested that soot and carbon black are formed from isotropic liquid droplets in which anisotropic mesophase is formed, with the distinction in orientation as compared to coke mesophase being due to the liquid-gas-phase interface. The observed disorder in the interior of the particle is attributed to distance from the liquid-gas interface that is believed to influence the ordering of the exterior.<sup>26</sup>



Figure 2-7. Schematic illustration of carbon black primary particle structure (A) and structure of the typical Brooks and Taylor mesophase sphere (B).<sup>26</sup>

Marsh<sup>26</sup> essentially suggested that since coke and carbon black are produced from the same aromatic petroleum pitch, it is likely that carbon black goes through a mesophase during carbonization like coke does. However, cokes are produced at mild temperature (~ 500 °C) as compared to soot and carbon black (~ 1,500 °C). Therefore, the PAHs and other hydrocarbons in petroleum pitch are vaporized and cracked both oxidatively and thermally during carbon black production. By the early 1990s, the soot community was largely in support of the HACA gas to particle mechanism.<sup>12,16–18,22</sup> The agreement found from simulations using this mechanism from many different flames and configuration should be regarded as a triumph for the combustion community given the complexity of the sooting processes.<sup>15</sup> Yet there are still a few well known and highly respected scientists who support the concept of carbon black and soot formation though mesophase.<sup>25,27,28</sup>

There may well be different formation mechanisms dependent upon both fuel and combustion process. Fuels with high PAH content may result in rapid particle nucleation with aromatic growth preceding fuel pyrolysis processes. Alternatively, at high concentrations and low temperatures the coalescence or condensation of PAHs may produce a mesophase with subsequent carbonization, akin to what Robert Hurt and others have proposed.<sup>27</sup> The mantra about acetylene driven PAH formation and subsequent growth via the HACA mechanism is only true for a limited range of conditions, certainly it is not universal. The HACA mechanism was developed based on simple laboratory models using a shock tube and gas jet diffusion flames burning simple gaseous fuels.

## 2.1.2.2 Soot and Carbon Black Nanostructure

Soot and carbon black exhibit a variety of structures ranging from nanoscale to microscale. Lattice structure measured on the nanometer scale is termed nanostructure.<sup>29</sup> Nanostructure

refers to the physical dimensions associated with individual graphene segments comprising the carbon material. Nanostructure metrics include length, curvature and spacing between opposing planes. Curvature may be measured by tortuosity or radii of curvature. Tortuosity may imply the presence of odd membered carbon rings within the aromatic framework.<sup>30– <sup>32</sup> Curvature is induced by the inclusion of isolated pentagons, heptagons, pentagonheptagon pairs, and the related Stone-Thrower-Wales defect.<sup>33,34</sup> The primary particles of soot and carbon black exhibit a nanostructure commonly referred to as core-shell structure. The outer shell is more ordered and arranged concentrically about the particle center, whereas the inner core consists of disorganized short lamellae. Nanostructure is often characterized by techniques such as Raman spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM). In contrast to XRD and Raman spectroscopy, high resolution TEM (HRTEM) can directly reveal the nanostructure with atomic scale resolution. Such HRTEM images provide a direct measure of the length, curvature, and orientation of the carbon lamellae.</sup>

Soot oxidation rates have been reported to have a wide variation. Vander Wal and Tomasek<sup>29</sup> used HRTEM to determine the oxidation rate of soot produced from different fuels based on a shrinking sphere model and found a strong dependence on initial nanostructure. The three soots investigated included soot formed from benzene, ethanol, and acetylene. The nascent nanostructures are shown in the HRTEM micrographs in Figure 2-8. The benzene soot exhibited short graphene segments with apparent lack of crystalline order (i.e. amorphous). Contrary to the benzene soot, soot formed from acetylene was comprised of extended carbon lamellae and in approximate parallel orientation with the surface of the particle. The ethanol soot had a high degree of curvature, such structures have been commonly been referred to as fullerenic-like. The term fullerenic-like should not be taken to imply fullerene related soot growth in the manner Kroto et al.<sup>21</sup> originally implied, but rather refers to curvature present in the individual graphene segments believed to be caused by five membered rings.



Figure 2-8. HRTEM micrographs of benzene (a), ethanol (B), and acetylene (C) soot.<sup>29</sup>

Not surprisingly the benzene derived soot was found to have a much higher oxidation rate than the acetylene soot, undoubtedly due to the higher relative number of active edge sites found in a material comprised of very short segments as compared to a more crystalline material. It has long been known that oxidation of the basal plane in graphitic crystallites is far lower than edge sites.<sup>35</sup> The ethanol derived soot had a fast oxidation rate, close to the benzene derived soot. The curvature in the ethanol samples is likely due to five membered rings and such curvature imposes bond strain and reduces the stability of the electronic resonance. The bond strain and out of plane bending leave individual carbon atoms highly susceptible to oxidation and thus curvature leads to increased rates of oxidation.<sup>29</sup> Not only did Vander Wal and Tomasek demonstrate the dependence of nanostructure on oxidation but clearly showed structure dependence on initial fuel species.<sup>29</sup>

Nanostructure analysis and quantification is routinely preformed with image analysis codes. Vander Wal et al.<sup>36</sup> developed image processing algorithms that extract fringe length, tortuosity and layer plane separation from HRTEM micrographs. The algorithms analyze many (i.e. 100-1000s) individual graphene segments from each primary particle. Most recently Wang et al.<sup>37</sup> have improved upon curvature analysis from the commonly used tortuosity measurement, which is simply the ratio of the length to the end-to-end distance along the curved lamellae. The improved quantification method determines the distributions of segment lengths, angles between segments, frequency of inflection points, relative inflection point locations, and overall angle changes for each fringe analyzed.<sup>37</sup> This level of detailed curvature analysis will be especially useful for identifying cases of undulating curvature (i.e. positive and negative curvature inflections).

### 2.1.3 Cokes and Mesophase

Carbonization of solid and liquid precursors results in the formation of either a coke or a char. A coke as defined by IUPAC<sup>5</sup>:

### "Description:

COKE is a solid high in content of the element carbon and structurally in the NONGRAPHITIC state. It is produced by pyrolysis of organic material which has passed, at least in part, through a liquid or liquid-crystalline state during CARBONIZATION. Notes:

As some parts, at least, of the CARBONIZATION product have passed through a liquid or liquid-crystalline state, the resulting NON-GRAPHITIC CARBON is of the graphitizable variety. From a structural viewpoint, the term COKE characterizes the state of GRAPHITIZABLE CARBON before the beginning of GRAPHITIZATION"

Coke passes through a liquid-crystalline state, this is the intermediate state between organic precursor and solid coke. Liquid crystals were first observed by Reinitzer in 1888 upon melting cholesteryl benzoate.<sup>38</sup> An opaque liquid was observed that cleared upon further temperature increase. Liquid crystals come in two broad classes: thermotropic liquid crystals that form upon heating and lyotropic liquid crystals that form from solution. The

lyotropic liquid crystals exist as micelles as an intermediate state between solution and precipitate. Lyotropic liquid crystals are dependent upon concentration. In the same manner thermotropic liquid crystals are dependent upon temperature.<sup>38</sup> Lyotropic liquid crystals are of great importance both scientifically and technologically. However, only thermotropic liquid crystals are applicable to carbonization (i.e. carbonaceous mesophase) and thus hereafter the term mesophase implicitly refers to a thermotropic liquid crystal phase. Additionally, carbonaceous mesophase differs from conventional mesophase in that carbonaceous mesophase is manufactured within the pyrolyzing pitch and is chemically active, whereas conventional mesophase can be produced and reversed at reproducible temperatures.<sup>28</sup>

In a liquid crystalline state, the molecules have sufficient ordering to account for the optical anisotropy, yet lack a crystal lattice (i.e. ordering is limited to one or two dimensions, not three). Mesophase is a term that has been adopted to describe the liquid crystal intermediate state. As such, mesophase is synonymous for liquid crystal and it is not accurate to define solid remnants of liquid crystals after cooling as mesophase. It is accurate and appropriate to characterize and describe the solid coke product based on the extent of mesophase development as observed under a polarized light microscope (i.e. optical texture).

The extent of mesophase development determines the textural quality of the resulting coke. The IUPAC<sup>5</sup> defines carbonaceous mesophase as:

"A liquid-crystalline state of pitch which shows the optical birefringence of disc-like (discotic) nematic liquid crystals. It is formed as an intermediate phase during thermolysis (pyrolysis) of an isotropic molten pitch. Generally, the spherical mesophase precipitated from a pyrolyzing pitch has the Brooks and Taylor structure. With continuous heat treatment the carbonaceous mesophase coalesces to a state of bulk mesophase before solidification to green coke with further loss of hydrogen or low-molecular-weight compounds."

From this definition, carbonaceous mesophase is defined as being nematic. Molecules, predominantly Polycyclic Aromatic Hydrocarbons (PAHs), possess one dimensional ordering in nematic mesophase and align parallel to one other. The discovery of the carbonaceous nematic mesophase is credited to Taylor, who in 1961 observed naturally occurring anisotropic spheres in the Wongawillie coal seam in New South Wales, Australia.<sup>39</sup> An igneous dyke had passed through the coal seam and slowly carbonized the wall of the coal seam over a kilometer distance. Taylor observed small anisotropic spheres in the vitrinite consistent with anisotropic stacking of lamellae parallel to the equatorial plane. The mesophase spheres grew in size at distances closer to the dyke and coalesced to form anisotropic coke.

The Brooks and Taylor structure is typically the structure of the mesophase spherules in which the aromatic lamellae stack parallel to the equatorial planar and curve toward the surface to meet the isotropic liquid at right angles as shown in Figure 2-9.<sup>40</sup>



Figure 2-9. Brooks and Taylor mesophase spherules structure<sup>40</sup>

The Brooks and Taylor mesophase spherules have been viewed by hot stage light microscopy and scanning electron microscopy (SEM). A SEM micrograph of early mesophase spherules is shown in Figure 2-10A<sup>4</sup> and a polarized reflected light micrograph of large mesophase spherules that did not coalesce into a state of bulk mesophase prior to solidification is shown in Figure 2-10B<sup>41</sup>. Once the mesogens form in liquid phase they begin to immediately associate. Thereafter the units coalesce into larger areas by continued polymerization and condensation reactions, forming anisotropic regions. An illustration of the stages of mesophase development are given in Figure 2-11.<sup>42</sup>



Figure 2-10. Scanning electron micrograph of mesophase spherules from decant oil  $(A)^4$  and polarized reflected light micrograph of mesophase spherules from decant oil  $(B)^{41}$ 



Figure 2-11. Stages of mesophase formation during the carbonization of decant oil.<sup>42</sup>

The mesophase formation is an irreversible process. As it develops, aromatic polymerization reactions are occurring simultaneously pushing the phase to a solid state. However, in 1971, Lewis<sup>43</sup> demonstrated via hot-stage optical microscopy that the initial mesophase formation is a reversible process, or more correctly, the discotic liquid-crystal property of mesophase can be reversible at early stages. Demonstrated by pyrolysis of naphthalene which produced anisotropic spheres at 350 °C, it was observed that upon rapid heating to 450 °C the mesophase spheres disappeared back into the pitch. When cooled back down to 350 °C the mesophase spheres reappeared. The reversibility was lost after only a few cycles.

Coke production is of significant industrial relevance. The U.S. Energy Information Administration reported that U.S. petroleum refineries produced 42 million metric tons of marketable petroleum coke in 2015 and another 9.3 million metric tons of metallurgic coke was produced from coal.<sup>44</sup> Delayed coking is employed by petroleum refineries often to minimize the yield of residual fuel oil via severe thermal cracking of feeds such as vacuum distillation residua. Prior to the evolution of delayed coking, severe thermal cracking of heavy feeds often resulted in unwanted coke deposits in the heaters. Undesired coke deposition results in more frequent and costly shut down time needed for decoking. As delayed coking evolved, it was determined that feed heaters could bring the feed to temperatures beyond the coking point without significant coke deposition in the heaters.<sup>45</sup> Reduction of coke formation in the heaters requires high velocity to reduce the retention time in the heater. The feed is rapidly heated and then charged to a large coking (soaking) drum, where it is provided with the long retention time needed for the thermal cracking reactions to reach completion. Thus, the process is appropriately named, Delayed Coking. The primary purpose of a delayed coker is to upgrade heavy bottoms into more valuable liquid products via a carbon rejection route. The rejected carbon is in the form of solid, carbon rich, petroleum coke. The process is semi-batch, employing at least two soaker drums that are switched from one to the other. Figure 2-12 shows a schematic flow diagram of a delayed coking process.


Figure 2-12. Schematic flow diagram of delayed coking process.<sup>45</sup>

Fresh feed is either charged directly to the furnace or more commonly to the fractionator. The coker feed is then rapidly heated to coking temperature between 480 and 515 °C by traversing through a gas fired furnace. The feed is then sent to the active drum that has been preheated by hot vapors, while coke is removed from the other drum. During the long residence time, exothermic condensation of aromatics along with heat from fresh feed provides the needed energy for the endothermic dealkylation and paraffin cracking. The condensed aromatics are converted to coke though the formation of carbonaceous mesophase. Two types of coke are produced from delayed coking of vacuum distillation residua and termed after their appearance: shot coke which resembles bee-bee shots is comprised of agglomerates of discrete hard spherules ranging in diameter from 0.2 to 0.5 cm, and sponge coke which resembles a sponge. Sponge coke undergoes a more extended mesophase than shot coke and results in a sponge like appearance with irregular lumps and pores. The optical texture of a sponge coke is displayed in the polarized light micrograph in Figure 2-13B. Shot coke is primarily used as a low value fuel. Sponge coke is also often used as fuel but can be used in the production of carbon anodes if the sulfur and metal content are below the specifications. Shot coke forms from rapid hardening of the mesophase which extinguishes growth of ordered structure, the optical texture of a shot coke is displayed in the polarized light micrograph in Figure 2-13A. Shot coke is common when coking a feed rich in asphaltene content. Shot coke can also occur when the feed is not homogeneous.

A specialty grade coke is made from the delayed coking of fluid catalytic cracking decant oil under different conditions compared to those used for coking of vacuum residua. The coke produced is a more crystalline coke known as needle coke. Needle coke is used to manufacture graphite electrodes for the recycling of scrap metal in an electric-arc furnace. Like shot and sponge coke, needle coke also derives its name from its physical appearance of needle like elongated crystalline microstructures. The optical texture of a needle coke is displayed in the polarized light micrograph in Figure 2-13C. Needle coke is highly graphitizable upon graphitization heat treatment. The graphitizability of needle coke is due to the rudimentary parallel stacking of planar molecules (PAHs). Feedstocks used for producing needle coke have consisted of decant oils, and pyrolysis tars derived from petroleum or coal. The key difference in needle coke feedstocks and vacuum residues used to produce shot and sponge coke lies in the aromatic content. As measured by Proton Nuclear Magnetic Resonance, decant oils have a total hydrogen-aromatic content between 20-35% where vacuum residues only have around 4%.<sup>46</sup> Vacuum residues contain more aliphatic hydrocarbons which increase the rate of carbonization due to easy cleavage of long aliphatic chains. A large increase is observed in mesophase development when the ratio of aromatic to aliphatic is increased.<sup>46</sup> Vacuum residues are chemically very reactive and produce low quantity and quality cokes as compared to the delayed coking of decant oils. Needle coke has desired properties that make it an excellent raw material in the production of graphite electrodes such as low coefficient of thermal expansion, low electrical resistivity, and high mechanical strength.



Figure 2-13. Polarized light micrograph of shot coke (A), sponge coke (B), and needle coke (C).<sup>42,46</sup>

The shot coke optical texture in Figure 2-13A is of the mosaic type. Mosaics describes small structures of anisotropic units that are 0.5-1 0  $\mu$ m in diameter (i.e smallest resolvable optical textures in a light microscope). Domains (often further classified as small and large) refer to anisotropic regions with diameters between 10-60  $\mu$ m, like the optical textures present in the sponge coke micrograph.<sup>42</sup> Elongated domains that are greater than 60  $\mu$ m in length and greater than 10  $\mu$ m in width are called flow domains.<sup>42</sup> The optical texture of sponge coke is often heterogeneous, comprising a mixture of optical textures with different levels of anisotropy from mosaics to flow domains.<sup>42</sup> A preponderance of a given texture, or a mixture of needle cokes, consists mostly of flow domains. Sponge cokes, display a predominance of acicular, or twisted flow domains and large domains. Shot coke texture is predominantly mosaics and some small domains. On the two extremes of the optical texture scale, needle cokes result from a high degree of mesophase development, whereas

shot cokes display an inhibited mesophase development.<sup>42</sup> Although mosaics are the smallest optical texture observed in a light microscope due to resolution, sub-micron mesophase is present in the isotropic pitch as displayed in the micrograph obtained via dark field Transmission Electron Microscopy (TEM) in Figure 2-14. Therefore, mesogens are never in "solution" in the liquid pitch.<sup>4,47</sup>



Figure 2-14. Dark field transmission electron micrograph of sub-micron mesogens.<sup>47</sup>

The mesophase development during carbonization depends upon the chemical constitution of the feedstocks. As a general relationship, an increase in the degree of aromaticity of the feedstock results in an increase in the principal optical texture size of the resultant semicokes.<sup>46</sup> There are notable exceptions to this general trend.<sup>46</sup> The mechanisms of phase change from isotropic pitch to anisotropic coke are not exactly known as the study is difficult because of the elevated reaction temperature (i.e. 400-600 °C) as well as the complexity of the molecular composition within the pitch.<sup>28</sup> The carbonization of model compounds is a way to simplify the study of mesophase development as compared to common coke feedstocks derived from petroleum and coal that contain several hundred individual compounds.

In 1957, well before Taylor discovered mesophase spheres in the Wongawillie coal seam, Walker was investigating the chemical composition of early carbonization products from model PAHs with the assumption that those species are intermediates in the process.<sup>48</sup> Anthracene was one such model compound and was selected because it was known to produce a highly graphitizable carbon.<sup>48</sup> The intermediate pitch PAHs were extracted from the anthracene derived tar pitch with benzene, separated using chromatographic techniques and identified with ultraviolet absorption spectroscopy. Large PAHs such as bisanthene were not identified as would be expected assuming that the main reaction occurring is condensation as was the consensus and still is today.<sup>4,28,43,47,48</sup> It is more likely that such large (i.e. 7 and 8 membered ring) aromatics are not extracted by the solvent and/or are not separated using chromatographic techniques. Intermediate species identified included 9,9'-bianthracene and isomer 1-1', both of which are expected to yield bisanthene upon further heating and hydrogen elimination, as illustrated in the reaction mechanism in Figure 2-15.<sup>48</sup>



Figure 2-15. Reaction mechanism of anthracene condensation.

Some decades later and with the benefit of the discovery of the carbonaceous mesophase, the above mechanism is often used as a simplified generalization for illustrating carbonization as seen in Figure 2-16.<sup>43</sup> Figure 2-16 gives a full picture of carbonization and subsequent graphitization of the resulting anthracene coke.



Figure 2-16. General reaction scheme for carbonization and subsequent graphitization.<sup>43</sup>

Carbonization of even a single PAH is far more complicated than the model reaction in Figures 2-15 portrays. For instance, Lewis<sup>43</sup> identified several dimeric molecules formed from anthracene carbonization as shown in Figure 2-17.



Figure 2-17. Reaction products from pyrolysis of anthracene.<sup>43</sup>

However, most lack proper steric conformation for additional dehydrogenation to yield a fully condensed PAH comprised only of six member rings.<sup>49</sup> Thus, the major (i.e. most stable) condensed PAH formed from the dimeric molecules is bisanthene and the formation of the intermediate 9,9'-bianthracene will far exceed other isomers due to the higher reactivity at the 9 position of anthracene.<sup>43,49</sup> Further dehydrogenation of bisanthene leads to additional condensation and polymerization reactions. Resulting in large PAHs that align parallel due to dispersion forces and form the anisotropic mesophase.<sup>49</sup> It is for this reason that anthracene has a well-developed mesophase and is highly graphitizable. According to Walker,<sup>49</sup> the nature of mesophase is dependent upon the following:

- 1. The extent of planarity of intermediate compounds formed
- 2. Rates of carbonization
- 3. Fluidity and extent (duration) of fluidity of liquid phase
- 4. Possible effect of solids on mesophase formation and coalescence

Using three model compounds, he and coworkers were able to elucidate the importance of the above items one and two in the carbonization process. The three model compounds were anthracene, phenanthrene (an isomer of anthracene), and biphenyl. Structure and numbering of these compounds are illustrated in Figure 2-18.



Figure 2-18. Structure of anthracene (I), phenanthrene (II), and biphenyl (III).<sup>49</sup>

Anthracene, a linear PAH, carbonizes much faster than its isomer phenanthrene, a branched PAH, as has been known since 1958.<sup>50</sup> The thermal reactivity differences are best understood by comparing the free valence indices of carbon atoms by position as it has been shown that carbonization reactivity increases with increasing free valence indices.<sup>49</sup> Free valence indices for anthracene and phenanthrene are given in Figure 2-19.<sup>49</sup>



Figure 2-19. Free valence indices of anthracene and phenanthrene.<sup>49</sup>

From the above indices it is apparent that the 9 and 10 position in anthracene has the highest values of either PAH. This position is expected to possess the highest reactivity for dehydrogenation and free radical formation and this is consistent with the observed higher carbonization reactivity as compared to phenanthrene.<sup>43,49</sup> Additionally, the magnitude spread of free valence indices is greater in anthracene and thus, the reaction pathway will predominantly proceed via the 9 and 10 position, whereas competing kinetic pathways will impact the mesophase development in phenanthrene due to the similarities in free valence indices by carbon position. Due to the high reactivity at position 9, anthracene carbonization forms 9-9'-bianthracene as an intermediate to bisanthene as previously illustrated in Figure 2-15. Phenanthrene will loss hydrogen and form free radicals at its most reactive sites, 9/10 and 1/8. Subsequent polymerization occurring at these reactive sites may yield the planar structure given in Figure 2-20.<sup>49</sup>



Figure 2-20. Possible structure from carbonization of phenanthrene proceeding via fusing the 9 and 1 positions.<sup>49</sup>

Such a well ordered planar structure would likely be a graphitizable carbon. However, since the free valence indices at position 4 are nearly equivalent to positions 9 and 1, free radical formation at 4 is likely to occur at an important rate.<sup>49</sup> Polymerization at positions 1 and 4 or 4 and 9 would not produce fully condensed planar molecules.<sup>49</sup> If free radicals formed at phenanthrene positions 2 and 3, a dimer of phenanthrene (i.e. biphenanthrene) would form as shown in Figure 2-21.



Figure 2-21. Structure of non-graphitizable biphenanthrene formed through reaction at the 2 and 3 position of phenanthrene.<sup>49</sup>

The biphenanthrenes formed by reaction between position 2 and 3 results in molecules that exhibit free rotation around a carbon-carbon single bond. Molecules with free rotation around a carbon-carbon single bond retard mesophase development and produce nongraphitizable carbons.<sup>51</sup> Since the activation energy needed to form a free radical at positions 2/3 is higher than 9/10 and 1/8, it is likely that with increasing temperatures the formation of biphenanthrene via reaction at position 2 and 3 will increase and have a greater contribution to the overall carbonization of phenanthrene as compared to lower temperature carbonization.<sup>49,51</sup> Therefore, it would be expected that the graphitizability of the coke produced from phenanthrene would decrease with increasing carbonization reaction temperature and indeed this was demonstrated by Peters et al.<sup>51</sup> The deleterious effect of carbon-carbon single bonds and free rotation between aromatics is based upon the model compound biphenyl. Carbonization of biphenyl results in an isotropic non-graphitizable carbon.<sup>43,49,51</sup> Walker and colleagues also co-carbonized anthracene and phenanthrene with biphenyl to observe potential retardation of mesophase development and resulting graphitizability by its introduction.<sup>49,51,52</sup> The anthracene-biphenyl system produced a coke of in-homogeneous optical texture with regions that were similar to pure anthracene and pure biphenyl carbonization. The phenanthrene-biphenyl system exhibited greater homogeneous texture and the observed optical texture of the anisotropic regions dropped sharply with increased additions of biphenyl. The in-homogeneous texture from anthracene-biphenyl and the homogenous texture from phenanthrene-biphenyl is likely due

to the differences in carbonization reactivity between the compounds. Biphenyl carbonization reactivity is three orders of magnitude less than anthracene and similar to phenanthrene at 450  $^{\circ}$ C.<sup>49</sup> Thus, explaining the observed textures, anthracene likely finished carbonization before biphenyl had a chance to influence mesophase and actively participated with phenanthrene carbonization.

Clearly, carbonization is a complex reaction process as illustrated by the insightful yet simplified studies on model compounds. It was shown that not only does the planarity of the PAH play an important role but so does the reactive site location and overall carbonization reactivity. The differences in carbonization reactivity in complex petroleum fractions like vacuum distillation residua can be taken advantage of and used to increase mesophase development by thermal pretreatment prior to carbonization is often inversely related to mesophase development.<sup>54</sup> Therefore, with lower temperature thermal pretreatment the more reactive shot coke precursors can selectively be initiated with little reaction of the bulk feed material. Low temperature pretreatment eliminates reactive species through self-condensation and thus allows for mesophase development to proceed unhindered at higher reaction temperatures.<sup>53</sup> Polarized light micrographs illustrating the increased mesophase development as observed by the improved optical texture from thermal pretreatment prior to carbonization residua are shown in Figure 2-22.



Figure 2-22. Light micrographs of direct carbonization of vacuum distillation residua (a), and carbonization after low temperature thermal pretreatment (b and c).<sup>53</sup>

Direct carbonization as displayed in Figure 2-22a, produced a texture similar to that of shot coke. Thermal pretreatment caused a substantial increase in optical texture as seen in Figures 2-22 b and c. The presence of mesophase spheres in Figure 2-22c is evidence that

the carbonization rate was considerably retarded due to pretreatment and corresponding mesophase development was enhanced.<sup>53</sup> This work utilized the different carbonization reaction rates of the feedstock components to extend the fluidity of the mesophase during carbonization, Walker's 2<sup>nd</sup> (reactivity) and 3<sup>rd</sup> (extent of fluidity) mesophase control criteria as listed previously.<sup>49</sup>

Coke microstructure (optical texture) depends on the extent of mesophase development and a degree of fluidity of the carbonizing medium is required to promote higher extents of mesophase development. Prolonging the fluidity during early carbonization allows the mesogen molecules to align and form a well-developed mesophase that covers a large area. The chemical reactivity directly impacts the viscosity (fluidity) of the carbonizing medium. Highly reactive mediums will result in rapid growth and increased viscosity, hindering parallel alignment and coke quality. Viscosity changes with heat treatment are depicted in Figure 2-23. Once the mesophase becomes so large, it loses mobility and allows for easier cross-linking between stacked mesogen molecules, thus increasing the viscosity in the final stages of carbonization as seen in Figure 2-23.<sup>4</sup>



# Heat treatment temperature

Figure 2-23. Viscosity change with heat treatment<sup>4</sup>

Producing semi-coke from carbonization of decant oil as a precursor to needle coke and studying the chemical composition of decant oil, Eser and colleagues have repeatedly observed that oils with higher concentrations of the PAH pyrene results in extended fluidly of the carbonization medium and a well-developed mesophase.<sup>41,55,56</sup> Pyrene functions as a hydrogen shuttler and a good solvent, extending fluidity and moderating the reactivity of the carbonizing medium. A proportionately large abundance of pyrene and methylated pyrenes have been shown to be characteristic of feedstocks that produce premium needle cokes.<sup>57</sup> Semi-coke is defined by IUPAC as:

## "Description:

SEMICOKE is a carbonaceous material intermediate between a fusible mesophase pitch and a non-deformable GREEN COKE produced by incomplete CARBONIZATION at temperatures between the onset of fusion (of coal, **ca.** 620 K), and complete devolatilization. SEMICOKE still contains volatile matter."

## 2.1.4 Char

Like coke, a char is formed from carbonization of solid and liquid carbon precursors. A char as defined by IUPAC<sup>5</sup>:

#### "Description:

CHAR is a solid decomposition product of a natural or synthetic organic material. Notes:

If the precursor has not passed through a fluid stage, CHAR will retain the characteristic shape of the precursor (although becoming of smaller size). For such materials the term "pseudomorphous" has been used. Some simple organic compounds, e.g. sugar, melt at an early stage of decomposition and then polymerize during CARBONIZATION to produce CHARS."

The key distinction between a coke and a char is that a char does not pass through a mesophase during carbonization. Considering that the graphitizability of a coke was shown to be highly dependent upon the extent of mesophase development during carbonization, it should come as no surprise that chars are non-graphitizable as they have no mesophase development. A char is an isotropic material that shows no optical texture representative of anisotropy when observed under a polarized light microscope. Isotropic chars are formed from carbonization of materials that are macromolecular in nature, e.g. cellulose or lignin components of biomass and specific cross-linked structures (C-O-C bonding) such as those found in low rank coals.<sup>58</sup> Synthetic resins like phenolic resin, polyfurfuryl alcohol (PFA) and polyvinylidene chloride are of a similar macromolecular nature and form nongraphitizable chars upon carbonization.<sup>58</sup> Char precursors are highly cross-linked initially or develop cross-linkages during the earliest phases of carbonization. The cross-linking is the material trait of the carbon precursor that results in char upon carbonization. For instance, cellulose and resins are cross-linked polymers as starting material, a linear polymer like polystyrene produces no char or carbonaceous residue, the process being one of depolymerization and chain scission.<sup>59</sup> Whereas crosslinked polystyrenes produce appreciable quantities of char upon carbonization.<sup>59</sup> Thus, condensation reactions compete with chain scission from crosslinked polystyrene.<sup>59</sup> Polystyrene is crosslinked by copolymerizing styrene (i.e. vinylbenzene) with divinylbenzene.

### 2.2 Heat-Treatment-Temperature

Upon heat treatment, carbon materials (i.e. non-graphitic carbons) transform towards their thermodynamically stable graphitic structure.<sup>47,60</sup> Non-graphitic carbons represent a broad and encompassing class of materials as defined by IUPAC<sup>5</sup>:

#### "Description:

NON-GRAPHITIC CARBONS are all varieties of solids consisting mainly of the element carbon with two-dimensional long-range order of the carbon atoms in planar hexagonal networks, but without any measurable crystallographic order in the third direction (c-direction) apart from more or less parallel stacking. Note:

Some varieties of NON-GRAPHITIC CARBON convert on heat treatment to GRAPHITIC CARBON (GRAPHITIZABLE CARBON) but some others do not (NON-GRAPHITIZABLE CARBON)"

From this definition, non-graphitic carbons are further broken down into graphitizable and non-graphitizable carbons. IUPAC<sup>5</sup> definitions for Graphitizable Carbon, Non-Graphitizable Carbon, and Graphitization Heat Treatment follow respectively:

"GRAPHITIZABLE CARBON is a NON-GRAPHITIC CARBON which upon GRAPHITIZATION HEAT TREATMENT converts into GRAPHITIC CARBON."

"NON-GRAPHITIZABLE CARBON is a NON-GRAPHITIC CARBON which cannot be transformed into GRAPHITIC CARBON solely by high-temperature treatment up to 3300 K under atmospheric pressure or lower pressure."

"GRAPHITIZATION HEAT TREATMENT is a process of heat treatment of a NON-GRAPHITIC CARBON, industrially performed at temperatures in the range between 2500 K and 3300 K, to achieve transformation into GRAPHITIC CARBON."

Upon graphitization heat treatment, graphitizable carbons will restructure into the graphite lattice. The unit cell of graphite is given in Figure 2-24. Graphite is comprised of graphene sheets with parallel alignment in the *ABABAB* stacking sequence that are weakly held in place by van der Waals attractions. The interatomic distance is 1.42 Å and the unit cell dimension in the a-axis direction is 2.46 Å. The spacing between graphene layers A and B is the  $d_{002}$  spacing of 3.354 Å.



Figure 2-24. Unit cell of graphite.

Thermodynamically, the carbon material being heat treated should proceed towards a more stable structure, one with a lower free energy. During graphitization heat treatment, disordered graphitizable carbons transform into graphitic carbons. As thermal annealing proceeds, the size of the graphene layers and crystallites grow and thus the energy of activation increases continuously. Therefore, higher temperatures are required as the material goes through increasingly longer length scale changes.

Heat treatment of carbon materials formed through carbonization go through several structural transformations as they approach a graphitic structure. These transformations require a given and progressive amount of input energy, often reported as Heat-Treatment-Temperature (HTT). Carbonized materials are formed at temperatures far lower than graphitization temperature. Thus, material transformations occur upon thermal annealing at temperatures well below the graphitization threshold temperature. Both low and high temperature annealing are of importance and have received a lot of attention by the carbon community. A detailed quantification of HTT and resulting material annealing was provided by Oberlin in 1984 and illustrated in Figure 2-25.<sup>47</sup>



Figure 2-25. Heat-Treatment-Temperature diagram.<sup>47</sup>

The smallest building block of the material in this model is the so called Basic Structural Unit (BSU).<sup>47</sup> The BSUs are small few layer stacks of PAHs with approximate parallel alignment. A BSU is formed as soon as two mesogens (molecules which form mesophase) associate forming the smallest anisotropic liquid crystal.<sup>4</sup> Such BSUs have been imaged using dark field TEM as displayed in Figure 2-26. These materials were prepared from kerogen and pitch (i.e. immature carbonaceous material). In dark field mode, the contrast is diffraction related. The BSUs in Figure 2-26A are less than 1 nm and distributed at random. With such small sizes, the BSUs in Figure 2-26A could be perceived as large PAHs. However, if the BSUs in Figure 2-26B at positions 5 and 16. The dark field TEM micrograph was taken using the 002 diffracted beam with use of an aperture and thus proves that the BSUs are stacked and not individual PAHs.



Figure 2-26. Dark field transmission electron micrograph of BSUs (A), electron diffraction pattern from BSUs (B).<sup>47</sup>

While mesophase acts primarily to align many BSUs into the observed optical texture, there is some growth of the BSU by attachment to other mesogens during mesophase development. The measured molecular weight of mesogens as often reported can be in excess of 1000 amu, a value that varies in the literature from 300 to 2500 amu.<sup>4,38,39,43,58</sup> Thus, the PAHs comprising the BSUs from a semi-coke may be larger than those in Figure 2-26A. This is a subtle point as the diagram of HTT is still accurate because it does not define the carbon basal plane length (La) of the BSU. Following immature carbonization, Oberlin studied single mesophase spheres and spheres that had semi-coalesced prepared by thin sectioning. Polarized light micrographs and 002 lattice fringe TEM images of the single and semi-coalesced mesophase spheres are provided in Figure 2-27.<sup>47</sup>



Figure 2-27. Polarized light micrographs of single and semi-coalesced mesophase spheres, A and B respectively. 002 lattice fringe dark field TEM micrographs from single and semi-coalesced mesophase spheres, C and D respectively.<sup>47</sup>

The 002 lattice fringes imaged from the single mesophase sphere are well aligned with high stacking order and parallelism. Upon coalescence, the short range order is partially destroyed and replaced by nematic order.<sup>47</sup> Oberlin states that the initial BSUs of the pitch (Figure 2-26A) are restored upon mesophase sphere coalescence and thus the domains of bulk mesophase are made of individual BSUs oriented nearly parallel.<sup>47</sup> Following the semi-coke stage of an anthracene derived semi-coke, all material transformations based on HTT were visualized using TEM. With increasing HTT a successive improvement in texture leading to crystalline order is produced by the steps illustrated in Figure 2-25.<sup>47</sup> In stage 1 single BSUs are present, they associate face to face into distorted columns in stage 2.<sup>47</sup> Columns coalesce into wrinkled layers in stage 3 and the distorted layers stiffen, become flat and perfect in stage 4.<sup>47</sup> The four stages (temperature dependent) are separated by "very rapid" transitions.<sup>47</sup> Just how rapid, no one knows.

From the bulk mesophase stage (i.e. semi-coke) to a HTT of 600 °C there is no observable material change, the BSUs remains small (i.e. La around 1 nm and stacked in layers of 2-3).<sup>47</sup> Between HTTs of 600 and 1,500 °C the BSUs have little increase in diameter. However, small columns of fringes are formed as illustrated by arrows in Figure 2-28 and stacking increases to approximately 10 layers. The material is turbostratic at this stage. Turbostratic structure is that of carbon layer planes with rudimentary stacking, but no correlation between adjacent layers.<sup>61</sup> That is the layers are not in the graphitic ABAB stacking, but are displaced by small translations parallel to the plane.<sup>61</sup> The so called ideal turbostratic spacing is 3.44 Å and is the shortest spacing prior to the layers moving into the AB stacking with interlayer spacing of 3.354 Å.<sup>2,7,60–63</sup> It has been demonstrated that there exists an apparent minimum La value of 10 - 15 nm necessary for a carbon material to transition from turbostratic columns as they are in stage 2 of Oberlin's diagram will not take on a three dimensional crystal lattice without first increasing in diameter and thus defining a minimum graphitic crystallite size restriction.



Figure 2-28. HTT and material transformation as illustrated by TEM for an anthracene coke.<sup>47</sup>

The next stage is initiated at temperatures greater than 1,500 °C where distorted columns quickly coalesce into stacks of distorted layers with observable increases in both Lc and La. The distorted layer planes can be characterized as wavy or wrinkled and are still turbostratic at this stage. As seen in Figure 2-28, increasing HTT from 1,600 to 1,800 °C acts to flatten the layer planes, yet electron diffraction and XRD do not indicate progression from turbostratic to graphitic structure. It is in the final stage (HTT > 2,100 °C) where complete de-wrinkling of the layers occur accompanied by a decrease in interlayer spacing.<sup>47</sup>

In the same study, Oberlin also investigated a wide range of carbon materials, not just the highly graphitizable anthracene semi-coke used to derive the HTT diagram. Oberlin made a very important observation and in her own words,

"All our studies on various carbonaceous materials show that there is no gap in the continuous variety of sizes of bulk mesophase elemental domains, for example from a few micrometers in pitch down to 50 Å in glassy carbons."

It is this observation that allows Oberlin to state that:

1. All non-graphitic carbons follow the same steps, although partial in the case of non-graphitizing carbon, during the graphitization process.

2. Graphitization proceeds "rapidly" according to HTT

3. The lower the extent of mesophase development, the lower the ability to graphitize upon heat treatment.

In the same year (1984), Marsh and Crawford published their findings in regard to the structure of graphitizable carbon as a function of HTT using high resolution TEM.<sup>64</sup> Their results are similar to that of Oberlin's and are best summarized visually in a cartoon of thermal annealing as function of HTT, shown in Figure 2-29.<sup>4,58,64</sup>



Figure 2-29. Cartoon of structural changes in a graphitizable carbon as a function of HTT.<sup>64</sup>

## **2.3 Graphitization Kinetics**

The very insightful work of Oberlin covered in the previous section was based on thermodynamics alone (i.e. temperature) and kinetics were not identified. Little attention has been directed towards graphitization kinetics because effects are small in comparison to maximum treatment temperature.<sup>65</sup> In fact, most studies on structural changes during heat treatment only provide HTT, with nothing mentioned about time above of temperature.<sup>2,4,43,47,60,62,64</sup> Needless to say, the difficulties in measuring kinetics of solid-state reactions at temperatures above 2,000 °C are most challenging experimentally. The

experimental challenge is in the control of achieving short time durations at precise elevated temperatures.

The classical kinetic analysis as applied, for example, to chemical reactions, requires measurements of reactant and product species concentrations with time. This approach is not applicable for graphitization as there is no distinct graphite phase growing from a disordered phase. Rather, the defects are ironed out in favor of order and therefore the process is akin to homogeneous order-disorder phenomena. Nonetheless, the process of graphitization does proceed monotonically toward a state of structural perfection and the concept of degree of graphitization is a meaningful measure.<sup>66</sup> The common parameter to measure when assessing the degree of graphitization is the  $d_{002}$  spacing as it can be measured accurately and is a good representation of graphitization, considering the process of graphitization can be defined as the development of three dimensional order from a two dimensionally ordered carbon. Therefore, the ideal kinetic study of graphitization would measure the  $d_{002}$  spacing in situ under isothermal heat treatment. Such measurements are technically feasible using in situ XRD as has been demonstrated by Fitzer and Weisenburger.<sup>67</sup> However, such measurements at elevated temperatures are plagued by the c-axis thermal expansion of graphite at graphitization heat treatment temperatures.<sup>61</sup> The  $d_{002}$  spacing increases by nearly 10% when heated to 2,500 °C, whereas the decrease in spacing due to graphitization (measured at ambient temperature) is only about 2%.<sup>61</sup> This complication cannot be accounted for, rendering in situ XRD measurements not useful for kinetic studies, because the c-axis thermal expansion coefficient is a function of carbon crystalline perfection (i.e. not easily removed as exact knowledge of structure and thermal expansion is required).<sup>61</sup>

With in situ kinetic measurements ruled out due to the unknown material properties at elevated temperatures, the next best kinetic study is an isothermal heat treatment versus time. The ideal heat treatment would bring the sample to temperature instantaneously, remain constant for a desired duration, and then instantaneously cool to ambient.<sup>61</sup> Such a heating scheme is not possible but has been approximated by either direct resistive (Joule) heating<sup>68</sup> and by rapid sample insertion into preheated graphitization furnaces. Joule heating may result in temperature non-uniformity with sample preparation and experimental configuration being challenging.<sup>61</sup> Due to the configurational difficulty involved in Joule heating and sample retention, the rapid insertion technique has historically received more attention. The observed time-temperature profiles can be corrected for heat-up and cool-down effects and temperature fluctuations to obtain an effective isothermal treatment time if thermally activated graphitization is a single activation energy step ( $\Delta H$ ).<sup>61</sup> Fischbach suggests accurate  $\Delta H$  values can be obtained by uncorrected data because of very high effective  $\Delta H$  values greater than 200 kcal/mole, thus transient times at moderate temperature (e.g. less than 2,200 °C) can be ignored.<sup>61,66</sup>

## **2.3.1 Rapid Furnace Insertion**

The study of graphitization kinetics appears to have had its beginning in 1961, or it was at least brought to the attention of the carbon community at that time, when two papers on

the topic were presented at the Fifth Conference on Carbon at Penn State University. Fair and Collins<sup>65</sup> presented their study on  $d_{002}$  spacing decrease and change in electrical resistivity in a calcined petroleum coke heated between 2,000 and 3,000 °C for durations as short as 8 minutes and as long as 20 hours. The samples were preheated to 800 °C by keeping them in the end of a resistance tube furnace and then rapidly inserting them into the hot center. Upon insertion, the furnace dropped 10 °C and recovered in seven minutes (i.e. it took seven minutes to heat the sample from 800 °C to the HTT used). The data obtained for the effect of time at temperature on interlayer spacing from their study is given in Figure 2-30.<sup>65</sup>



Figure 2-30. Interlayer spacing of a petroleum coke vs. time at temperature.<sup>65</sup>

They report, that interlayer spacing reaches a minimum value at a given HTT. Suggesting that effective energy of activation of the graphitization process is constantly increasing as graphitization advances. However, based on the their plot (Figure 2-30) it would appear that if the time axis (x-axis) could be stretched way out, the interlayer spacing would continue to decrease from all of the above HTTs observed. If the spacing keeps decreasing upon time above temperature that would suggest the possibility of a single activation energy for graphitization. Since very little three dimensional ordering takes place at temperatures below 2,000 °C, the activation energy for this process clearly has an initial threshold value. The question is whether it is progressively increasing or if a singular activation energy is applicable with the process then being kinetically controlled. The second paper on graphitization kinetics presented at the fifth Conference on Carbon was by Mizushima, who also studied a petroleum coke and reported similar results, increasing activation energies which were found to range from 75 kcal/mole at 1,400 °C (sub-graphitization temperature) to 210 kcal/mole at 2,200 °C.<sup>69</sup>

In 1963, Fischbach<sup>66</sup> demonstrated that graphitization kinetics of a petroleum coke at temperatures in the range of 2,300 - 2,700 °C can be represented by a superposition of first-order rate processes and that the effective activation energy is constant and equal to approximately 250 kcal/mole. This value was in excellent agreement with the 260 kcal/mole activation energy previously found for graphitization of pyrolytic carbons.<sup>70</sup>

Thus, Fischbach determined that there is not a temperature dependent limit on degree of graphitization attained by thermal heat treatment, but a kinetic restraint. Fischbach described graphitization kinetics as a collection of first-order processes with a broad distribution of rate constants and a single activation energy. The distribution of rate constants is so broad that at any one temperature only a portion of the graphitization process is observed after multiple hours of heat treatment, making the determination of an effective rate constant at a given temperature difficult.<sup>66</sup> Fischbach collected layer plane spacing data very similar to that of Fair and Collins, Figure 2-30. However, Fischbach was able to superimpose the curves by translating along the time axis as shown in the composite curve in Figure-2-31.



Figure 2-31. Composite curve for petroleum coke graphitization.<sup>66</sup>

The composite curve in Figure 2-31 was created by translating the 2,500 °C and the 2,700 °C curves to join smoothly with the 2,300 °C curve. The arrows represent the translation (time shift) of the higher temperature curves required to smoothly join to the 2,300 °C curve. The composite curve suggests that if treatment times at 2,300 °C were extended to about two years, the  $d_{002}$  would reach graphite layer plane spacing.<sup>66</sup> For this reason, synthetic graphite producers elect to use high temperature graphitization heat treatment. The Acheson process for synthetic graphite production calls for heating at 3,000 °C for a duration of twenty hours.

In 1969, Murty et al.<sup>71</sup> set out to resolve the controversial problems in graphitization kinetics (single or distribution of activation energies?). They collected layer spacing from a commercial calcined petroleum coke after graphitization heat treatment with respect to time at various temperatures, shown in Figure 2-32.



Figure 2-32. Inter layer spacing of a commercial calcined petroleum coke with respect to time at temperature.<sup>71</sup>

Murty et al.<sup>71</sup> utilized the degree of graphitization (g) as originally defined by Franklin<sup>3</sup> and provided in Equation 2-1, with a modification - the minus 1 added to this expression so that g approaches zero as graphite layer spacing is achieved.<sup>71</sup>

$$g = (3.440 - 3.354)/(3.440 - d_{002}) - 1$$
[2-1]

Where g is the degree of graphitization, 3.440 Å is the nominal disordered turbostratic spacing (disordered carbon can have much larger spacing, but graphitization does not include layer spacing decreases outside of the range starting at 3.440 Å),  $d_{002}$  is the measured layer plane spacing, and 3.354 Å is the graphitic layer plane spacing. Using g as the kinetic parameter Murty et al. provide the following empirical equation to follow kinetic changes at any temperature:

$$g = \alpha t^{-n} \tag{2-2}$$

Where  $\alpha$  and n are constants and t is time. Murty et al. provided the following plot of log g and log t.



Figure 2-33. Isothermal plot of log g vs. log t.<sup>71</sup>

From Figure 2-33 it is seen that Equation 2-2 is applicable. Using values of  $\alpha$  and t from least square fits, the g values were calculated from Equation 2-2 and those g values were used in Equation 2-1 to find d<sub>002</sub>. The calculated d<sub>002</sub> are in excellent agreement with the measured values (thus validating Equation 2-2). The lines in Figure 2-32 are calculated and the points are measured values. The instantaneous rate of graphitization dg/dt is then the derivative of Equation 2-2 with respect to time:

$$dg/dt = -n\alpha t^{-(n+1)} = n\alpha^{-1/n} \times g^{1+1/n}$$
[2-3]

Rewriting Equation 2-3 in logarithmic form:

$$\log(dg/dt) = \log(n - 1/n) \times \log(\alpha) + (1 + 1/n)\log(g)$$
[2-4]

The  $\alpha$  term was found to obey the relation, where  $E_a$  is activation energy and R is the gas constant:

$$\alpha = \alpha_0 \times e^{Ea/RT}$$
 [2-5]

The plot  $\log(\alpha)$  vs. 1/temperature is given in Figure 2-34.<sup>71</sup> The origin of the ordinate is shifted for each petroleum coke sample for clarity. The validation for Equation 2-5 is provided by the straight line in Figure 2-34.<sup>71</sup> Equation 2-6 is from the substitution of Equation 2-5 in Equation 2-4.

$$\log(dg/dt) = \log(n) - \frac{1}{n} \times \log(\alpha_o) - (E_a/nRT) + (1 + 1/n)\log(g)$$
[2-6]



Figure 2-34. Plot of log  $\alpha$  vs. 1/temperature for the three coke heat treated by Murty et al.<sup>71</sup>

If graphitization has a distribution of  $E_a$  values, it must be a function of the degree of graphitization (g).<sup>71</sup> From Equation 2-6,  $E_a$  can be continuously increasing or decreasing with g if n is also continuously increasing or decreasing with temperature.<sup>71</sup> Therefore, if n is a continuous function of temperature then  $E_a$  is a continuous function of g and graphitization is comprised of distribution of activation energies.<sup>71</sup> If n is independent of temperature,  $E_a$  is independent of the extent of transformation (g) and graphitization is a single valued activation energy process.<sup>71</sup> The term n showed no regular or continuous temperature dependence as illustrated in Figure 2-33, where n is the slope of the line log(g) vs. log(t) at constant temperature.<sup>71</sup> From the above analysis by Murty et al.<sup>71</sup> graphitization is found to be a single valued energy of activation process.

Since these pioneering studies in the 1960's on graphitization kinetics using rapid insertion into preheated furnaces, the topic was closed until the 1990's when technological advances lead to highly controlled experimental apparatus for direct resistive heating.

## 2.3.2. Direct Resistance Heating

By the late 1990s, direct heating experimental apparatuses had come a long way since the 60s and sample collection was less of an issue than it had been in the past. Shim and Hurt<sup>72</sup> who were interested in studying the oxidation reactivity reduction of coal char on the timescales relevant to suspension fired combustion systems, designed a direct heating apparatus capable of heating coal to 2,400 °C for durations as short as two seconds. The heating device is shown schematically in Figure 2-35. The sample was held between two thin graphite sheets to assure good contact (uniform heating) and for the purpose of sample collection. The graphite sheets act as resistance heaters and were held in place by brass electrodes connected to a DC power supply. The setup is similar to wire mesh heaters, but enables higher temperatures without contamination by metallic elements and potential catalytic reactions. One disadvantage is the coals can't be directly heated as received because volatile material evolution makes sample retention a challenge. Rather, the coals were carbonized at 700 °C for 1 hour and are the starting materials for direct heating.<sup>72</sup>



Figure 2-35. Schematic of direct resistance heating device.<sup>72</sup>

Temperature of the lower graphite sheet was measured by a pyrometer and based on onedimensional heat transfer, it was determined that the sample reached the graphite sheet temperature in approximately 50 ms.<sup>72</sup> An anthracite coal (Lykens Valley #2) and a bituminous coal (Pocahontas #3) were obtained from the Penn State Coal Sample Bank and chars from the two coal samples were heated for two second durations at 1,700 and 2,400 °C. HRTEM results are shown in Figure 2-36.



Figure 2-36. HRTEM micrographs of Lykens valley #2 anthracite coal char HTT 700 °C - hold time 1 hour (Top Row): virgin (A), HTT 1,700 °C - hold time 2 seconds (B), HTT

2,400 °C - hold time 2 seconds. HRTEM micrographs of Pocahontas #3 bituminous coal char HTT 700 °C - hold time 1 hour (Bottom Row): virgin (D), HTT 1,700 °C - hold time 2 seconds (B), HTT 2,400 °C - hold time 2 seconds.<sup>72</sup>

It is interesting to note that the starting bituminous char is more ordered than the anthracite char, see Figures panels 2-36 D vs. A. Although micrographs of the virgin coal were not provided, it is well known that structural order increases with rank (i.e. anthracite is more ordered than bituminous). Thus, the higher order in the staring chars is attributed to mesophase development preferring the more hydrogen rich and mobile PAHs in the bituminous coal. It would appear that the anthracite liquid transition state occurs at higher temperatures. Upon rapid heating to 1,700 °C and 2,400 °C and holding for two seconds the anthracite sample transformation to a more ordered structure is significant. Fringe length as measured using image analysis increased from 2 nm from the virgin char to 3 nm at 1,700 °C and to 4 nm at 2,400 °C, all while tortuosity decreased. The bituminous char apparently changed very little upon rapid heating, an average fringe length of 3 nm was observed from Figures 2-36 D, E, and F. The ordering even appears to decrease from char heated at 1,700 °C and char heated at 2400 °C. Traditionally, HTT based experiments (i.e. long duration isothermal heating) have shown that many cokes reach a first Lc maximum and spacing minimum followed by degradation with increasing HTT and then re-establish order upon much higher HTT.<sup>43,64</sup> For instance Marsh<sup>64</sup> found that the Lc for coal is typically less than 1 nm and increases to 2.3 nm at an HTT of 525 °C. This increase in ordering is the first maximum in structural development as increasing HTT to 650 °C results in an observed reduction of Lc to 1.5 nm. Above 1,100  $^{\circ}$ C a progressive increase in Lc is always observed from HTT based experiments. The first maximum of structural order is a result of mesophase development. The retrograde step can be explained by considering the initial nearly parallel alignment of the PAHs after mesophase development that then bond to neighbors which may not be in the same preferred orientation with increasing HTT.<sup>64</sup> Upon increased HTT the energy is provided to align the larger graphene layers. The rapid heating results of Shim and Hurt<sup>72</sup> show that these two materials have very different kinetic behavior and that the annealing steps are far from complete even in the anthracite sample. This is an exciting observation given that much of the annealing transformation rate is thus bounded and can be systematically studied, a far more interesting observation than something always occurring faster than is observable.

## 2.4 Graphitizing and Non-Graphitizing Carbons

The most thermodynamically stable form of carbon at standard pressure is graphite. Due to the extremely high activation energy barrier, many disordered structures are metastable at standard temperature and pressure. Crystalline disorder or total lack of order, amorphous, is common among synthetic carbons formed from carbonization. These materials evolve toward ordered graphite when heated to graphitization temperature. The graphitization process has been a subject of extensive investigation for the past century. The most famous of which is that by Rosalind Franklin. In 1950, she interpreted XRD patterns of graphitizable carbons upon heat treatment up to 3,000 °C. Her insights have resulted in the

present-day method to quantify and understand the extent of graphitization.<sup>3</sup> The three staring carbon materials included two commercial cokes, a petroleum coke and a needle coke, and a coke produced from polyvinyl chloride. The three cokes were calcined at 1,000 °C for two hours and the layer plane spacing after calcination was 3.44 Å, the same for all three materials. Therefore, her hypothesis was that graphitizable carbons exist with spacing of 3.44 Å when the structure is perfectly non-graphitic, and 3.354 Å when perfectly graphitic.<sup>3</sup> This meant that there was not a continuum in spacing, but rather the spacing "jumps" down from 3.44 to 3.354 Å when converting to perfect graphite from turbostratic graphite. It should be mentioned that disordered carbons can have layer plane spacing much larger than 3.44 Å and values of 3.8 Å are common among many non-graphitic carbons that were subject to low temperature and/or rapid formation. The 3.44 Å represents a "perfectly disordered" (i.e. turbostratic graphite) structure where the disorder lies in the caxis. It is this transition from 3.44 to 3.354 Å that is taken as the graphitization process and the prior annealing steps correspond to pre-graphitization thermal annealing. If Franklin is correct in that layer plane spacing is restricted to 3.44 or 3.354 Å and not a continuum then one would expect to resolve these two peaks with XRD, rather than find a single broad peak suggestive of continuum spacing. Two peaks would be present if crystallites of particular spacing concentrated into separate regions. However, if the two are randomly distributed a singular broad peak would be observed and the peak would be representative of a weighted average. Franklin provided the following Equation:

$$d_{002} = 3.354 + 0.086p$$
 [2-7]

Where p is the probability of random disorientation (layer plane spacing of 3.44 Å) between any two neighboring layers and 0.086 is the spacing difference between disordered and ordered. Thus, p is 1 when all layers are spaced 3.44 Å apart and 0 when all layers are 3.354 Å apart. For Franklin's hypothesis to hold, there must be a linear relationship between p and  $d_{002}$ . However, as seen in her original plot in Figure-2-37 the experimentally measured layer spacing did not follow a linear relationship with p.



Figure 2-37. Franklin's original plot of p vs. layer plane spacing.<sup>3</sup> Circles are experimentally measured layer spacing.

To reconcile the experimental curve and hypothesized relation (straight line in Figure 2-37) deviation, Franklin suggested that there exists a transition layer with intermediate spacing between ordered and disorder regions.<sup>3</sup> If a transition layer does exist then  $d_{002}$ spacing would equal:

$$d_{002} = 3.44 - k(1-p) - 2k'p(1-p)$$
[2-8]

Where k is the difference in spacing between ordered and disordered, 0.086 Å, and k' is the unknown transition layer spacing reduction relative to 3.440 Å. Upon fitting it was found that k' is equal to one half of k and therefore the transition layer spacing is half way between graphite and turbostratic graphite. The result supports the hypothesis of a transition layer. Moreover, the decrease in spacing at the transition might be distributed among two or three neighboring disorientations rather than concentrated in the first.

In 1951, Franklin used XRD to study the crystallite growth in both graphitizable and nongraphitizable carbons.<sup>60</sup> Graphitizable carbons included the three cokes that were previously used to study graphitic carbon structure: polyvinyl chloride  $((C_2H_3Cl)_n)$  coke, petroleum coke, and needle coke. Additionally, a coking coal was identified as a graphitizable carbon. The non-graphitizable carbons included the oxygen rich: low rank coals, sucrose char (i.e. sugar char), and char produced from polyvinylidene chloride  $((C_2H_2Cl_2)_n$ . All materials were carbonized at 1,000 °C for a duration of 2 hours. Differences in the two classes of material are evident even prior to graphitization heat treatment, the non-graphitizable carbons have Lc heights accounting for only two layers per stack where the graphitizable carbons have four layers per stack. Low angle X-Ray scattering can be used to compare relative porosity and Franklin observed high porosity in the non-graphitizable carbons and relatively low porosity in the graphitizable carbons. Franklin observed that compact carbons (i.e. cokes) are graphitizable and porous carbons are non-graphitizable.<sup>60</sup> The fine structure porosity was assessed by comparison of densities, Table 2-1.

Material	Density [g/cm <sup>3</sup> ]
Non-graphitizable	
Polyvinylidene chloride	1.59
Sugar char	1.72
Graphitizable	
Polyvinyl chloride	1.99
Petroleum coke	2.00
Needle Coke	2.06

Table 2-1. Densities of graphitizable and non-graphitizable carbons.<sup>60</sup>

Where a lower density corresponds to a higher porosity. Franklin concludes that porosity is built in during early carbonization and locked in placed by rigid cross-linking and the cross-linking is preserved on heating. Such cross-linking is believed to hinder the coalescence of stacks and impart a random orientation with respect to one another. The compact graphitizable carbons are much softer than the hard non-graphitizable carbons as is easily observed simply by grinding with a pestle and mortar. Considering that the individual crystallites in either material are soft graphite the hardness of non-graphitizable carbons is attributed to the greater strength of bonding (cross-linking) between neighboring crystallites.<sup>60</sup>

Franklin suggested that cross-linking is favored in the presence of oxygen or by a shortage of hydrogen. The hydrogen shortage example is seen in polyvinyl chloride  $((C_2H_3Cl)_n)$  and polyvinylidene chloride  $((C_2H_2Cl_2)_n$ . Polyvinylidene chloride has only enough hydrogen to remove the Cl as HCl and no surplus to improve the fluidity of the carbonizing medium. Upon carbonization of Polyvinylidene chloride at only 220 °C, a solid product is formed. Polyvinyl chloride produces tar and no solid product when carbonized at 220 °C. The additional hydrogen in polyvinyl chloride acts to extend the fluidity and thus allows for formation of a graphitizable compact coke, whereas polyvinylidene chloride has no such fluid state and thus forms a non-graphitizable highly porous cross-linked char. Franklin was essentially describing mesophase development, the key to synthetic graphite, although the discovery of carbonaceous mesophase would not occur for another decade. A schematic representation of graphitizable and a non-graphitizable carbon is illustrated in Figure 2-38.<sup>60</sup>



Figure 2-38. Schematic representations of graphitizable carbon (A) and non-graphitizable carbon (B). $^{60}$ 

Both material classes show an initial increase in layer diameter, La, at the expensive of amorphous carbon. Once La is greater than 2.5 nm, Lc begins to increase. Lc increases more so and faster in the graphitizing carbons than in the non-graphitizing carbons. The graphitizing carbons relax into the graphitic lattice and resulting  $d_{002}$  spacing, whereas the non-graphitizing carbons resist spacing reduction even when heated to 3,000 °C. Additionally, the La found after graphitization heat treatment was on the order of 50 nm from graphitizable carbons and only 7 nm from non-graphitizable carbons.<sup>60</sup> Lc values corresponded to less than ten layers per stack from non-graphitizable carbons after graphitization heat treatment and more than 30 layers per stack from graphitizable carbons. A detailed study of crystalline growth in both the La and Lc direction as a function of HTT for graphitizable and non-graphitizable carbon was provided by Emmerich in 1995 and displayed in Figure 2-39.<sup>73</sup>



Figure 2-39. Variation of La and Lc as a function of HTT for graphitizable and non-graphitizable carbons.<sup>73</sup>

The turbostratic model is still a useful way to characterize disordered carbons and is probably the most widely used model still today. The model is based on stacking disorder. However, it has become increasingly clearer that defective layer planes must also be considered to accurately characterize non-graphitizable carbons. Franklin's original nongraphitizable model is broadly correct, but the key to her model lies in the cross-links and the structure of these cross-links was unknown, thus the key to non-graphitizing behavior is not adequately explained. Some early works, like that by Ergun and Teinsuu in 1959, suggest that sp<sup>3</sup> hybridized carbon is responsible for non-graphitizing behavior.<sup>74</sup> The presence of sp<sup>3</sup> hybridized carbon in non-graphitizable carbon was based on an analysis of XRD patterns that appeared to suggest the presence of tetrahedral diamond like domains, this was used to explain the high hardness of many non-graphitizing carbons.<sup>32,74</sup> However. the presence of sp<sup>3</sup> hybridization in carbon after graphitization heat treatment is most unlikely as it is not stable at elevated temperature and standard pressure. Diamond itself is converted to graphite at 1,700 °C.<sup>31</sup> Ruland<sup>75</sup> found that reconciling the (002) XRD peak of graphitic structure from tetrahedral sp<sup>3</sup> is challenging, ultimately Ruland concluded that non-graphitizable carbon XRD patterns are inconsistent with tetrahedral carbon.75 Furthermore, it is unlikely that the cross-links responsible for non-graphitizing behavior are aliphatic type sp<sup>3</sup> carbon chains as they would not be sufficiently rigid to prevent graphitization at elevated temperature.<sup>76</sup> Additionally, neutron density studies on nongraphitizable carbons have determined that the material is comprised entirely of sp<sup>2</sup> hybridized carbon after graphitization heat treatment. More recently, Electron Energy Loss Spectroscopy (EELS) in the TEM has found that non-graphitizable carbons are greater than 80% sp<sup>2</sup> and convert to 100% sp<sup>2</sup> upon graphitization heat treatment.<sup>77</sup>

The development of High Resolution-TEM (HRTEM) in the late 1960s and early 1970s made direct imaging of the non-graphitizable carbon structure possible, thus model atomic level structures could be based on direct visualization rather than interpretation of diffraction patterns. One, of the earliest models of carbon based on HRTEM observation was provided by Heidenreich et al. in 1968.<sup>78</sup> The purpose of this work was to test the resolving power of a transmission electron microscope as this was very early on in the development of High Resolution TEM. High Resolution is reserved for atomic layer plane resolution that is made possible by phase contrast, an interference pattern of the diffracted and transmitted electron beams and primary image contrast used to resolve detail below 1 nm. Although TEM is typically thought of as diffraction contrast imaging, phase contrast imaging is still involved at lower magnifications as well. Heidenreich et al.<sup>78</sup> determined that a carbon black heat treated to graphitization temperature provided the best sample to test TEM resolving power. This sample was selected because of the following: known layer plane spacing of 3.4 Å as measured by XRD, stability under the beam, and that the material is inherently thin. Heidenreich et al. were successful in resolving the 3.4 Å layer plane spacing. From their HRTEM images they provided a model for the structural transformation of carbon black upon graphitization heat treatment, shown in Figure 2-40. Crystallite growth in carbon black is restricted by geometry of primary particles.



Figure 2-40. Model of carbon black and carbon black heat treated to 2,600 °C based on HRTEM images.<sup>78</sup>

The structure of the heat treated carbon black can be described as a hollow polyhedron. The shell thickness is the Lc dimension and the La as would be measured in XRD is that of a single facet.<sup>78</sup> However, as shown the facets are connected at bent joints and thus the actual La is the entire particle circumference.<sup>78</sup> This illustrates a weakness in interpreting XRD patterns, as a stack of layer planes that are jointed (i.e. bent out of plane) do not contribute to the La value determined by XRD. Carbon blacks fall under the non-graphitizable category since they have turbostratic spacing of 3.44 Å even after graphitizable carbon based on direct HRTEM visualization. The reason for the non-graphitizability of this material is likely due to the geometry of the primary particle and thus it is somewhat different from the "classical" non-graphitizing carbons believed to be caused by excessive pre-existing cross-liking. It is the geometry of carbon black (i.e. quasi spherical) that leads to cross-linking of the facets upon heat treatment. As the BSUs flatten out and grow they join at high angles to form the closed shell polyhedrons.

A few years later, a model based on HRTEM observation was produced for glassy carbon by Jenkins and Kawamura in 1971.<sup>79</sup> Glassy carbon is a non-graphitizable carbon commonly used as an electrode in electrochemistry, crucibles for high temperature applications, and as a component in prosthetic devices.<sup>80</sup> Glassy carbon was first produced by General Electric in the early 1960s from cellulose and is named after its appearance, "glass-like".<sup>31</sup> Soon thereafter, it was produced form phenolic resin and polyfurfuryl alcohol (PFA).<sup>31</sup> Glassy carbon is a unique from of carbon in that it is impermeable to gases and extremely inert.<sup>31</sup> It has an extremely low oxidation rate, lower than any other form of carbon.<sup>81</sup> Glassy carbons are relatively unaffected by acids, whereas graphite is broken down almost completely in sulfuric and nitric acids. glassy carbon is unaltered even after subjection to acid for a duration of many months.<sup>80</sup> Based on a HRTEM study, Jenkins and Kawamura provided the following model of glassy carbon:



Figure 2-41. Jenkins and Kawamura model of glassy carbon.<sup>79</sup>

The model assumes that the polymeric precursor orientation is memorized and thus glassy carbon resembles a polymer in that the graphitic bands are made up of narrow twisted ribbons.<sup>79</sup> This model has been widely accepted, but Harris pointed out that such a structure with conjoined micro-pores would be permeable to gases and glassy carbon is highly impermeable.<sup>31</sup>

As it was now (early 70s) evident that HRTEM lattice-fringe imaging provided structural information that XRD could not, the non-graphitizing model development continued to advanced, but now based on HRTEM. In 1975, Ban et al. developed a model of non-graphitizable carbon based on polyvinylidene chloride heated to 2,700 °C, shown in Figure 2-42.<sup>82</sup> This model is very similar to the glassy carbon model of Jenkins and Kawamura, but differs in that there exists a large variation in crystallite width. It is comprised of two or three layer stacks that are highly twisted, branched, and enclose voids. This type of structure has been described as being ribbon-like.<sup>82</sup>



Figure 2-42. Model of polyvinylidene chloride char after graphitization heat treatment.<sup>82</sup>

The model was later criticized by Oberlin<sup>47</sup> as being based on false interpretation of HRTEM micrographs. The (002) lattice fringe images are only visible when the layer planes are parallel to the electron beam (i.e. satisfying Bragg diffraction) and as such the ribbon-like appearance in a micrograph could derive from a three dimensional cage like structure. Further criticism of the model pointed out that upon graphitization heat treatment the graphene layers would stiffen and appear folded, where the model represents the layers with smooth curvature. Such a structure would be unstable at elevated temperature.<sup>76</sup>

Burket et al. demonstrated that the barrier limiting graphitization of non-graphitizing PFA char could be overcome by partial activation (mild oxidation).<sup>83</sup> Activation removes disordered oxidation-susceptible carbon atoms and thereby reduces the graphitization barrier. Without the removal of the defect carbon atoms via oxidation they become partially stabilized during heat treatment by inducing curvature and thus limiting graphitizablity.<sup>83</sup> Defect carbon was assumed to be in the form of odd member rings. Others have suggested that such defects and cross-linking are predominantly due to oxygen content.<sup>84,85</sup> Nongraphitizability of oxygen rich precursors has provided the empirical evidence to formulate such a hypothesis. Rhim et al. have apparently detected approximately 5 atomic % oxygen remaining in chars after graphitization heat treatment.<sup>84-86</sup> Recently, McDonald-Wharry et al. have reviewed existing non-graphitizing char models and developed a revised model that incorporates key concepts from earlier models.<sup>84</sup> The updated model is named the "distorted graphene triad." The model is largely focused on persistent oxygen groups and progresses through three phases as shown in Figure 2-43. The three phases represented include an amorphous region that dominates at HTT below 500 °C, distorted graphene regions that consume the amorphous carbon with increasing HTT, and pristine graphene segments.



Figure 2-43. Schematic of virgin char (a) where grey is amorphous carbon and blue is distorted graphene. Char after subjection to HTT between 600-1,000 °C (b) and 1,500-2,500 °C (c).

The initial structure is dominated by amorphous carbon as illustrated by the grey regions in Figure 2-43a. The amorphous carbon regions are consumed by the growing distorted graphene segments represented by the blue regions and flat hexagonal graphene regions. The three step process as outline in Figure 2-43 is very similar to the quasi-percolation

model put forth by Rhim et al.<sup>85</sup> The added value of the Distorted Graphene Triad model can be seen in Figure 2-44 where an attempt is made to describe the structure of a distorted graphene segment that is wedged between three larger graphene segments that are growing towards each other forming the defect region.



Figure 2-44. Distorted Graphene Triad model.<sup>84</sup>

Where the three graphene layers are designated with a G and one of the defects is designated with a D. The role of this proposed "distorted graphene" phase was used to explain the curved cross-links connecting the BSUs and role of oxygen in non-graphitizable carbons.<sup>84</sup> The model presumes that the non-graphitizability of chars is due to persistent oxygen groups that distort the graphene layers at junction sites.

Oxygen is a leaving group even at temperatures well below that of graphitization heat treatment and thus it is highly unlikely that the distorted graphene region emphasized by McDonald-Wharry et al. would survive graphitization heat treatment.<sup>47</sup> The empirical evidence showing that high oxygen content precursors result in non-graphitizability may be better explained by Franklin's<sup>60</sup> original theory on hydrogen deficiency due to the removal of oxygen via H<sub>2</sub>O. Oxygen is also released in the form of CO and CO<sub>2</sub> and thus the radical left behind from the removal of a carbon atom from a six member ring may also play a role in non-graphitizability. For instance Vander Wal and collaborators have shown that the extent of soot curvature found from benzene derived soot increases with partial

premixing.<sup>87–89</sup> Partial oxidation of benzene was predicted to yield cyclopentadiene concentrations sufficient to realize visible curvature in soot nanostructure.<sup>87</sup> The reaction mechanism is shown in Figure 2-45.



Figure 2-45. Schematic of cyclopentadiene formation and induction into soot via decomposition of phenol.<sup>87,88</sup>

Partial premixing leads to the formation of phenoxy radicals. At flame temperature, phenoxy radicals decompose as oxygen leaves, taking a carbon atom along as CO and leaving behind cyclopentadiene that gets incorporated into the soot and induces curvature. Evidence of this is provided by the HRTEM micrographs of benzene soot with and without partial premixing as shown in Figure 2-46.



Figure 2-46. Soot nanostructure derived from benzene fuel with 0% (A), 10% (B) and 20% (C) oxygen doping.<sup>87</sup>

As seen in Figure 2-46, oxygen doping induces curvature. A pure benzene diffusion flame results in soot with a disordered center and a well-defined exterior with lamellae nearly parallel to the surface, 10% oxygen doping acts to reduce the order in the exterior in favor of curved lamellae, upon 20% oxygen doping the majority of lamellae have a high degree of curvature.

The discovery of the  $C_{60}$  Buckminsterfullerene, fullerene for short, in 1985 by Smalley, Kroto, and Curl.<sup>19</sup> and the fullerene-related carbon nanotube in 1991 by Iijima<sup>90</sup>, stimulated much research into the structure and properties of these carbon materials. The carbon

nanotube in particular, both single and multi-wall, possess extraordinary mechanical and electrical properties and are expected to have significant technological impact.<sup>31</sup> The knowledge gained from these materials has also provided fresh perspective into an old class of carbon material, chars.<sup>91,76,80,31,32</sup> The structure of fullerene and carbon nanotubes (CNTs) is illustrated in Figure 2-47. The key defining feature of fullerenes is the five membered pentagonal carbon ring.<sup>31</sup> There are twelve five membered rings distributed symmetrically in an icosahedral structure, where all five membered rings are isolated from one another by six membered rings. The carbon nanotube can be imaged by rolling up a sheet of graphene and capping the ends with half of a fullerene. The zig-zag nanotube results from fullerene end caps divided parallel to one of threefold axes.<sup>31</sup> The armchair nanotube is a result of dividing the fullerene along one of the fivefold axes.<sup>31</sup>



Figure 2-47. Schematic of zig-zag carbon nanotube and orientation of fullerene end caps (a) and an armchair carbon nanotube and orientation of fullerene end caps (b).<sup>92</sup>

Production of fullerene and CNTs from arc discharge of graphite electrodes is always accompanied by other carbon nanoparticles that are less perfect and not symmetric. Such particles include asymmetric multi-walled CNTs and faceted nanoparticles. These structures are shown in the HRTEM micrographs in Figure 2-48, taken from the work of Harris.<sup>31</sup>



Figure 2-48. Asymmetric multi-walled carbon nanotube (A) and a faceted carbon nanoparticle (B).<sup>31</sup>
The conical structure in Figure 2-48A is common and believed to the caused by a single pentagon at point X and a single heptagon at point Y is believed to cause the so called negative curvature (i.e. saddle point).<sup>31,80,91</sup> Single is somewhat misleading as the odd membered rings responsible for the points of inflection would if present exists in each layer in the c dimension, it is "single" only in the limit of a single layer plane in the La dimension. The onion like nanoparticle in Figure 2-48B has been referred to as a giant asymmetric multi-walled fullerene.<sup>91</sup> Where the facets are locked in place at the joints. These joints can be considered to be cross-linkages and are often considered to contain odd membered rings.<sup>31,91,93</sup> This idea of odd membered ring cross-links can be applied to non-graphitizable carbons and HRTEM has been utilized to examine chars and heat treated chars for the purpose of establishing whether fullerene-like structures are present.<sup>91,76,80,31,32</sup>

The difference in structure between graphitizing and non-graphitizing carbons is best illustrated using HRTEM. Figure 2-49 shows images from a non-graphitizable sucrose char and a graphitizable anthracene coke carbonized at 1,000 °C and subsequently heat treated at 2,300 °C, taken from the work of Harris.<sup>91</sup>



Figure 2-49. HRTEM images of a non-graphitizable sucrose char (A), a graphitizable anthracene coke (B), sucrose char after and anthracene coke after heat treatment at 2,300  $^{\circ}$ C (C) and (D) respectively.<sup>91</sup>

In the case of sucrose char (A), the structure, lack thereof, is totally isotropic as further demonstrated by the lack of directionality found in the Selected Area Electron Diffraction (SAED) pattern. Anthracene coke (B) has rudimentary parallel stacking of layer planes prior to graphitization heat treatment as seen directly in the bright field micrograph and displayed by the arc spots in the SAED pattern. Upon graphitization heat treatment, the anthracene coke readily coverts to highly crystalline graphite as seen in (D). In contrast multi-faceted nanoparticle are found in thermally annealed sucrose char, where the arrows in (C) represent a seven membered ring as the likely cause of the saddle point and negative curvature.<sup>31,91,93</sup>

The observation of fullerene-related nanoparticles in the sucrose char after graphitization heat treatment suggests that the virgin sucrose char may have contained fullerene-related structures (i.e. odd membered rings).<sup>91</sup> However, direct visualization of odd membered ring structures with HRTEM in chars prior to heat treatment is difficult as the material is amorphous and a degree of crystallinity is required for high-resolution phase contrast imaging. If odd membered rings were present it would help explain why these materials are non-graphitizing and have a fullerene-related nanostructure after graphitization heat treatment. Yet, it is possible that odd membered ring containing structures observed in HRTEM micrographs of non-graphitizable carbons after heat treatment are actually formed during the graphitization heat treatment at the junction points where growing layers meet.

From the apparent observation of odd membered rings found in heat treated char and the occasional observation of closed structures in virgin char, Harris developed a new model for virgin char, shown in Figure 2-50.<sup>91</sup> The model consists of small discrete curved layers with pentagons and heptagons dispersed randomly. Odd membered rings are predominantly five membered as the stability of a five membered ring is greater than that of a seven membered ring. The model suggests that the structure of non-graphitizing carbons is similar to fullerene soot, the disordered material formed on the walls during arc-evaporation from which  $C_{60}$  and other fullerenes are extracted.<sup>91</sup> Observation of pentagons and heptagons have been made from fullerene soot.<sup>94</sup> Graphitization heat treatment transforms fullerene soot into nanoparticles with striking similarity to those found in heated chars, thus supporting the contention that odd membered rings are present in the virgin chars and are the cause of non-graphitizability.<sup>91</sup>



Figure 2-50. Model of non-graphitizing carbon based on odd member ring structures.<sup>91</sup>

The char model proposed by Harris in Figure 2-50 does not use the BSUs as is commonly done, but rather discrete fullerene-like fragments are used to construct the nanostructure. There are likely some aliphatic cross-links randomly distributed between the fullerene-like fragments from chars produced at lower temperature carbonization that the model has omitted. Additionally, the model has omitted oxygen that is found in moderate amounts in some char formed by low temperature carbonization. For these, oxygen would be found on edge sites and as ether cross-links between the fullerene-like fragments.

Defect regions result in cross-linking and the observed non-graphitizability. The structure of such defects is still open for debate with the two leading models: the distorted graphene triad and the fullerene-related nanostructure claiming oxygen and odd membered rings responsible for defects, respectively. Until odd membered rings are directly observed via HRTEM from virgin char, the debate will continue.

## **2.5 Laser Annealing**

When a new form of energy is harnessed great advances typically follow. Controlling fire provided a massive advance for early man, coal and the steam engine ushered in the industrial revolution, electricity and the modern heat engine powered by petroleum have provided man with a high quality of life. Light Amplification by Stimulated Emission of Radiation (LASER) can provide extremely high coherent optical energy with high spatial and temporal control. It is therefore reasonable to expect lasers to be very impactful.<sup>95,96</sup> Stimulated emission was first harnessed into a working device by Charles Townes in 1954, with the invention of Microwave Amplification by Stimulated Emission of Radiation or MASER. Shortly after Charles Towns published the concept of the laser in 1958, Theodore

Maiman demonstrated the first working laser capable of producing coherent radiation in 1960, a ruby laser. Stimulated emission, the physics of laser radiation, was first predicted by Einstein in 1916 who showed that both spontaneous and stimulated emission are necessary to satisfy Planck's radiation law.<sup>95</sup> Since their discovery, lasers have been widely used in science and research, industry, and in everyday technology like the DVD player. Lasers can be utilized to precisely measure distances and the meter is now based on the speed of light emitted from a laser propagating through vacuum. Therefore, the National Institute of Standards and Technology no longer needs to guard one meter long platinumiridium bars. Lasers have been invaluable for testing the foundation of the exciting new world of quantum physics. For instance, the strange world of quantum physics states that two particles created at the same time and point in space are described by the same wave function. The particles are in a state of "entanglement." These two particles interact in such a way that their quantum states cannot be described independently of one another, even when separated by distance. This theory was not originally accepted, Albert Einstein and coworkers famous called the theory Spooky Action at a Distance in 1935.<sup>97</sup> Quantum theory implies that measurement of one particle immediately influences the other, even when separated by large distances. Quantum entanglement would not be measured experimentally until the development of the laser and the resulting ability to produce coherent photons in a state of quantum entanglement. Since the 1970s, lasers have been the source of photons used to measure and demonstrate quantum entangelment.<sup>98,99</sup> In such experiments, first proposed by John Bell in 1960, photons are separated by a distance and one is subject to a change in polarization and an opposite change is observed in the other.

The first ruby laser emitted red light at 694.3 nm. Today lasers are available with wavelengths spanning from extreme ultra-violet to long-wavelength-infrared. With wide wavelength availability, lasers have found use in diagnostics and characterization, in naming a few applications: laser induced fluorescence, laser induced incandescence, raman, coherent anti-stokes raman spectroscopy, interferometry, holography, laser induced mass spectroscopy, and laser induced breakdown spectroscopy. Lasers are now commonly used in material processing, predominantly for metals and are used to cut, weld, drill, clad, bend, etch, and etcetera. Additive manufacturing, also termed 3-D printing, is a rapidly developing process where complex 3-D objects are built up layer by layer from a metal powder bed by selected laser sintering. One example of this technology can be found in the new lean burn jet engines manufactured by General Electric that use complex fuel injectors produced entirely by additive manufacturing. Material processing utilizes the laser as a heat source and the laser provides the highest power density available to industry. For instance, a modest 2-kW continuous wave CO<sub>2</sub> laser focused down to 0.2 mm has a power density of 63,662 W/mm<sup>2</sup>, as compared to 500 W/mm<sup>2</sup> from an electric arc.<sup>95</sup> A Q-switched Nd:YAG laser with a pulse duration of 8 ns and pulse energy of 300 mJ focused down to 0.2 mm has a power density of  $1.2 \times 10^{12}$  W/mm<sup>2</sup>, this power density is equivalent to the summation of every operating power plant in the world (for 8 ns).<sup>95</sup> By expanding the beam the laser can also offer the lowest power density and anywhere in between.

Laser carbon synthesis techniques are commonly used to produce fullerenes and nanotubes. Fullerene was discovered by laser vaporization of graphite, although the electric arc discharge is now the main synthesis root.<sup>100</sup> Laser assisted CVD is often used in carbon nanotube synthesis to achieve higher spatial and temporal control by providing local heating (photo-thermal) or local photolytic molecular decomposition.<sup>100</sup>

Despite the wide use of laser processing in industry and laser synthesis of carbons, laser annealing of carbon material remains uncommon. Not surprisingly the majority of the limited work on laser annealing of carbons has been focused on CNTs.<sup>101–104</sup> Ma et al.<sup>104</sup> observed the formation of onion like nanoparticles after irradiating multi-walled CNTs with a continuous wave CO<sub>2</sub> laser. Zhang et al.<sup>103</sup> found that iron catalyst particles can be removed from double wall CNTs while preserving the structure of some of the double walled CNTs, presumably by self-healing of the carbon under laser radiation from a frequency tripled Nd:YAG laser (355 nm). Zhang et al.<sup>102</sup> also claim to "weld" bunches of double walled CNTs together with a CO<sub>2</sub> laser (although TEM observations suggested destroying CNTs and splattering amorphous carbon over remaining CNTs).

Flame formed soot has commonly been laser annealed since at least 1984 (and prior, starting in the 1970s with Raman spectroscopy) when Melton first demonstrated Laser Induced Incandescence (ILL) as a technique cable of measuring soot volume fraction and primary particle size in situ.<sup>105</sup> However, as a soot diagnostic tool annealing was never the central focus and is ignored for simplification of the energy balance. Incandescence is the emission of radiation from a hot body and is derived from the Latin word *incandescere*, which means to glow white or light from heat. The LII technique involves heating soot with a laser to temperatures well above the flame temperature and high enough to emit measurable quasi-black body radiation.<sup>106</sup> The incandescence signal is detected with a gated (time-integrated) device, often spatially for visualization of soot distribution in a flame or time-resolved for determination of primary particle size.<sup>106</sup> The wavelength distribution of the detected incandescence signal is used to determine temperature according to Planck's law. Temperature of the laser heated soot particles range from approximately 3,000 to 4,200 °C depending on laser energy.<sup>106–112</sup> At these elevated temperatures a number of processes are initiated that have impact on LII signal, an illustration of such processes are provided in Figure 2-51.



Figure 2-51. Illustration of heating and cooling mechanisms that have influence on temperature and LII signal from laser heated soot.<sup>106</sup>

The energy and mass balance given in Equation 2-9 is used to solve for soot volume fraction and particle size.

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$$\frac{dU_{int}}{dt} = Q_{abs} + Q_{rad} + Q_{cond} + Q_{sub} + Q_{ox} + Q_{ann} + Q_{th}$$
[2-9]

Where,  $U_{int}$  is internal energy, t is time,  $\dot{Q}_{abs}$  is absorptive-heating rate,  $\dot{Q}_{rad}$  is radiative heat loss rate,  $\dot{Q}_{cond}$  is conductive heat loss rate,  $\dot{Q}_{sub}$  is the evaporative cooling rate,  $\dot{Q}_{ox}$  is the oxidative heating rate,  $\dot{Q}_{ann}$  is heating rate from exothermic annealing, and  $\dot{Q}_{therm}$  is the thermionic cooling rate. Heating is provided by absorption of incident laser radiation. Oxidation is often ignored as the process is much slower and less significant than laser absorption. However, oxidative heating will work against conductive cooling at longer delay times and needs to be accounted for to determine cooling rates used for particle size determination. Initial cooling is dominated by mass loss (sublimation) when maximum temperature is in excess of 3,700 °C, an approximate vaporization temperature for carbon.<sup>113</sup> After the first tens of nanoseconds mass loss extinguishes and cooling proceeds predominantly via conduction. Radiative cooling is significantly less than conductive cooling at the temperatures used in LII and under normal and elevated pressure, radiative cooling is dominant in vacuum.<sup>106,114,115</sup> Lastly, thermionic emission has a negligible influence and is ignored in LII models.<sup>116</sup> The previous assumptions are valid as the ignored terms have little impact on heating or cooling. However, assumptions regarding

wavelength dependent emissivity and the complex index of refraction of soot have been highly debated.<sup>109,110,117,118</sup> The vast majority of the effort to determine wavelength dependent emissivity has focused on nascent soot (i.e. prior to laser heating). However, annealing has been reported to change the optical properties. Vander Wal et al.<sup>119</sup> demonstrated this via a two pulse experiment, where soot was heated twice in rapid succession with a two laser setup and differences in optical properties were observed between the first and second pulse. More recent studies have reported evidence that the optical properties change as inferred by scattering/extinction measurements.<sup>118</sup> The nanostructure change of soot particles under pulsed laser heating (i.e. annealing) as observed by HRTEM has been detailed by Vander Wal and coworkers<sup>107,119–121</sup> They found

that soot particles undergo structural transformations leading to shell-like and rosette structures due to laser heating. More recently Michelson et el.<sup>122</sup> reported similar findings regarding laser annealing of soot from LII measurements and observed newly created amorphous carbon particles formed from solidification of vaporized carbon.

Most recently, Gaddam<sup>123</sup> took advantage of laser annealing soot and demonstrated a potentially new diagnostic tool for the purpose of identifying soot source, Soot Source Identification by Laser Derivatization (SSILD). High resolution transmission electron microscopy has shown that the nanostructure of soot from different anthropogenic combustion sources varies, hence nanostructure may be used for identification of the carbon source.<sup>124</sup> However, such differences are subtle, even with enhanced image processing. Flame formed carbon from combustion is a non-equilibrium product and the nanostructure and underlying chemistry may retain the formation history. Accentuating the embedded nanostructure and underlying chemistry aids in differentiating the combustion origins of the carbon. To this purpose, Gaddam laser annealed soot using a wavelength of 1064 nm from a Nd:YAG laser. A single laser pulse from the Nd:YAG laser is 8 nanoseconds long, hence the carbon's total time above temperature was limited. In pulsed laser annealing, the transformations occur within nanoseconds while the carbon is at elevated temperatures. It is understood that the greatest energy barriers of the reactions, such as bond breaking occur within picosecond time scales, while longer-range motions such as reorientation of graphene segments occur on longer timescales. From laser heating time scales the extent of transformation is kinetically controlled by time above the threshold temperature for transformation. Therefore, the differences can be kinetically exploited. To resolve the detailed morphological and nanostructural changes HRTEM was used to examine the carbons before and after annealing.<sup>123</sup> Quantification of the HRTEM images by lattice fringe analysis provided several statistical metrics describing the nanostructure order. Gaddam demonstrated that SSILD was capable of differentiating materials with initial nanostructures indistinguishable from one another. Figure 2-52 shows HRTEM images of the starting structures, structures after laser annealing, and after furnace heating at 2,100 °C for a duration of 2 hours.



Figure 2-52. HRTEM images of R250 and diesel soot. Top row – R250 [(a) nascent, (b) laser - 250 mJ/cm<sup>2</sup>, 1 pulse, (c) furnace - 2,100 °C. Bottom row – Diesel soot [(d) nascent, (e) laser - 250 mJ/cm<sup>2</sup>, 1 pulse, (f) furnace - 2,100 °C.<sup>123</sup>

Laser heating was performed using a single pulse, fluence of 375 mJ/cm<sup>2</sup>, whereas furnace heating was performed in a conventional furnace at 2,100 °C for 2 hours. As displayed in Figure 2-52 laser heating leads to partial annealing and traditional furnace heating produces highly ordered polyhedral particles. It is seen that pulsed laser annealing accentuates the embedded nanostructure and underlying chemistry differences between the two nascent carbons. Upon laser heating the differences between the two carbons are largest, despite having very similar nascent nanostructure. Gaddam suggested that annealing trajectory initially proceeds in a divergent path dependent on the nanostructure and chemistry of the sample, but ultimately converges into an equivalent final structure.<sup>123</sup>

Laser annealing of carbon has been applied to CNTs and to a lesser extent to soot, but has not been applied to conventional forms of carbon like coke and char. One potential reason is that these are bulk materials, coke graphitization is typically done on a large scale where the equivalent laser setup would be technically challenging due to the limited skin depth of laser light. Still, there is huge potential for laser annealing thinner carbon materials, studying kinetics at very short time durations if observable, studying annealing trajectories especially from non-graphitizing carbons, and potentially developing novel materials.

# **Chapter 3**

# **Experimental**

### **3.1 Carbon Production**

Most carbon materials used in this study were produced via carbonization in sealed tube reactors, in a horizontal tube furnace, and via polymerization.

## 3.1.1 Coke and Char Production

Coke and char samples were prepared by carbonization in a tube bomb reactor. The tubing reactor illustrated in Figure 3-1 has an internal diameter 3/4 of an inch and an internal volume of 25 ml.



Figure 3-1. Schematic of horizontal tubing reactor.

Carbon precursors were held in an aluminum foil tube closed at both ends and fitted to the internal diameter of the reactor. The aluminum foil was filled with approximately ten grams of feed and inserted into the reactor and sealed. Before the reactor is plunged into a preheated sand bath it must be purged of oxygen. The reactor was connected to an ultra-high purity nitrogen manifold and pressurized to first check for leaks and then to purge oxygen. The pressurized nitrogen was slowly vented to the atmosphere. The reactor was pressurized and slowly vented at least three times, ensuring that oxygen was purged out. The reactors were then submerged into a preheated and aerated sand bath. Upon submersion, the preheated sand bath would drop in temperature down to 480 °C and recover to the set temperature of 500 °C in approximately five minutes. Vertical agitation of the reactors at a frequency of 100 oscillations a minutes and an amplitude of 2.5 cm was provided during

the isothermal heat treatment. Heating duration and temperature were typically fixed at 5 hours and 500 °C. However, longer durations up to 24 hours and temperatures up to 550 °C were required to complete the carbonization of fluorene. Carbonization occurred under autogenous pressure (i.e. no pressure control) and pressures reached between 1000 and 1500 psi. After the desired reaction period, the reactors were rapidly cooled by quenching in cold water. Once the reactors were cooled, the gases produced during the coking reactions were vented in a fume hood. Semi-coke bars and chars formed inside the aluminum foil were extruded from the reactor and carefully unwrapped. The samples were washed with dichloromethane to remove any liquid product and were left to dry in a fume hood overnight before subsequent characterization and annealing.

## 3.1.2 Carbon Black and Synthetic Soot

Carbon black used in this study was obtained from a commercial vendor. In addition to commercial carbon black, laboratory generated synthetic soot samples were produced in in a horizontal tube furnace. Carbon precursors were feed into the tube furnace as an aerosol, suspended with an argon carrier gas flow. The furnace was operated at 1,100 °C. Based on flow rate the approximate resonance time in the furnace is three seconds. Liquid carbon precursors were introduced to the furnace using a bubbler and argon carrier gas. Synthetic soot was collected at the exit on Whatman filter paper.

# 3.1.3 Polymer

The polymer polyfurfuryl alcohol (PFA) was used in this study. The PFA was prepared by dissolving p-toluenesulfonic acid monohydrate (0.048 g) (Sigma–Aldrich) in 5ml of Triton X-100 (Sigma–Aldrich) by mild heating. Five ml of furfuryl alcohol (99% Sigma–Aldrich) was then added to the solution. The reaction mixture was stirred magnetically until completion of polymerization.<sup>83</sup> The polymer was subsequently carbonized at 500 °C for five hours as described in Section 3.1.1.

## **3.2 Traditional Thermal Annealing**

Sub-graphitization heat treatment up to 1,200 °C was performed in a horizontal tube furnace under argon. Graphitization heat treatment was performed under argon in a Centorr Vacuum Industries series 45 graphitization furnace. The graphitization furnace was pumped down to at least 100 micrometers mercury and flushed with argon at least three times to remove oxidizer prior to heating. The furnace was heated at a rate or 25 °C a minute until maximum temperature and held at maximum temperature for an hour. The maximum acquirable temperature was 2,600 °C. Samples were held in graphite crucibles. Temperatures up to 1,400 °C are measured with a K type thermocouple, upon further temperature increase the thermocouple is extracted and temperature measurements are taken with a pyrometer through a view port. Between temperatures where both the pyrometer and the thermocouple are operable, the agreement was within 3 °C. Samples were removed from the furnace after cooling overnight.

#### 3.3 Laser Annealing

Samples were laser annealed with two different lasers: and a Q-switched Nd:YAG laser and a continuous wave  $CO_2$  laser. The lasers provide extremely rapid heating, followed by fast cooling and therefore kinetics and trajectories of thermal annealing can be explored and exploited.

For annealing to occur laser light must be absorbed which depends on the absorption coefficient of the material. The infrared (IR) laser wavelengths like those used here (i.e. 1064 nm and 10.6  $\mu$ m), can excite free electrons within a metal, or vibrations within an insulator. In semiconductors both electronic and vibrational excitations are possible.<sup>125</sup> The resulting non-equilibrium electronic distribution rapidly thermalizes via electron–electron and electron–phonon interactions, quickly transferring energy to lattice phonons.<sup>126</sup> The time it takes for the excited electronic states to transfer energy to phonons and thermalize is material specific. In general the thermalization time is  $10^{-12} - 10^{-10}$  s for metals and slightly slower for non-metals. The excitation energy is dissipated to heat in a timescale far faster compared to any other timescales involved in the process.<sup>126</sup> Therefore, laser annealing is equivalent to heat addition in the absence of ablation and/or vaporization.

A laser can be broken down into three basic components: the lasing medium, pumping source, and optical resonator. The lasing medium is most often a solid crystal or a gas. For a lasing medium to lase a population inversion is required between energy states (electronic or vibrational) and such a population inversion is created by pumping up the excited energy states. Pumping sources for solid state laser are typically flash lamps, but can be other lasers. Gas lasers are often pumped with direct current or radio frequency (RF). As lasing atoms (Nd) or molecules (CO<sub>2</sub>) relax through a radiative process, the photon emission can be spontaneous or stimulated. Spontaneous emission lifetimes depend on the stability of the excited state. The photons emitted by spontaneous emissions have random directionality and are not useful in laser design, except to initiate stimulated emission. Stimulated emission is the reverse of absorption, when a photon on resonance strikes the already excited medium, stimulated emission occurs. The photon released has the same frequency, phase, polarization, and propagation direction as the photon that induced stimulated emission.<sup>95</sup> The optical resonator is used to reflect laser light back through the lasing medium for the purpose of amplification via stimulated emission, while the pumping source maintains a population inversion between the upper and lower energy states. The optical resonator or cavity is simply two mirrors place at the ends of the lasing medium where one is only partially reflective and thus allows for laser output.

#### 3.3.1 Nd:YAG Laser

A 10 Watt Q-switched Contiumm Surelite-III Nd:YAG laser was used in this study. YAG stands for yttrium aluminum garnet ( $Y_3Al_5O_{12}$ ) and Nd is the element neodymium, the ion that produces stimulated laser radiation (Nd<sup>3+</sup>:YAG). Approximately one percent of the yttrium atoms are replaced with neodymium ions in a Nd:YAG laser. Excitation of the

electronic states of the Nd ions are responsible for lasing. Lasing occurs between upper laser energy level 3 and lower laser energy level 2, from the four level system as depicted in Figure 3-2.



Figure 3-2. Nd:YAG laser energy level diagram.

Two flash lamps are used to excite the Nd ions. The flash lamps are quartz tubes filled with krypton gas. A hot plasma is formed upon discharge of electric current. The plasma emits radiation peaked between 800 and 900 nm that matches absorption bands of Nd and causes excitation of Nd ions. The transition from level four to level three is rapid and nonradiative. Energy level three is meta-stable allowing for population inversion to build up between levels two and three, as transition from level two to level one is also fast and nonradiative. The stimulated laser emission wavelength ( $\lambda$ ) is 1064 nm. This laser has built in harmonic generators capable of frequency doubling ( $\lambda$ =532nm), tripling ( $\lambda$ =355nm), and quadrupling ( $\lambda$ =266nm) the laser output. However, only 1064 nm was used in this study. Shorter wavelengths were not utilized to avoid exciting spectral interferences such as fluorescence or phosphorescence when measuring laser induced incandescence (LII) singal.<sup>127</sup> Shorter wavelengths are also more likely to cause material ablation, which is undesired when focus is on thermal annealing.<sup>106,128</sup> The near-IR 1064 nm laser light also has the advantage of increased skin depth and Rayleigh range. For laser heating to occur uniformly, the Rayleigh size regime ( $\pi d/\lambda < 0.3$ ) must be satisfied. For 1064 nm laser light the Rayleigh range is approximately 102 nm. When this criterion is satisfied, absorption occurs volumetrically and the sample is uniformly heated. The skin depth is the depth at which incident laser light intensity has decreased by 1/e and can be approximated by the following equation:

$$\delta = \sqrt{\frac{2}{\omega\mu\sigma}} = \sqrt{\frac{2}{(1.76 \times 10^{15} \, rad/s)} \times (1.256 \times 10^{-6} \frac{N}{A^2}) \times \left(1 \times 10^{5} \frac{s}{m}\right)} = 95 \, nm \quad [3-1]$$

Equation 3-1 is used to approximate the skin depth for a good electrical conductor.<sup>129</sup> Where  $\omega$  is angular frequency of the laser light,  $\mu$  is permeability of free space, and  $\sigma$  is electrical conductivity of the material. Using the electrical conductivity of graphite in Equation 3-1, results in a skin depth of 95 nm. Skin depth decreases with increasing electrical conductivity and thus disorganized carbon with lower electrical conductivity will have a deeper skin depth. Skin depth decreases significantly with a decrease in laser light wavelength.

As a Q-switched laser, the pulse duration is fixed and is 8 nanoseconds (ns). A Q switched laser utilizes an acoustically or most often an electrically controlled optical shutter or Pockels cell. The shutter is placed between the crystal and the output mirror. Sound waves and electric current can temporarily change a materials index of refraction. Therefore, when switched on, light is deflected from the path it would have taken. Q-switches exploit this phenomenon to switch a laser beam on and off. When the shutter is closed there is no feedback from the mirror and the laser beam cannot amplify. The flash lamps are still pumping Nd atoms from the ground state and disposing them into the excited state, but since there is no stimulated emission the population inversion keeps building. When the inversion is built to a high value and shutter opened, the spontaneous emission is then able to reflect from the output mirror and amplify the medium. Due to the high population inversion the gain will grow very quickly. The amplifying beam consumes the population inversion, which then decreases rapidly. When the shutter is suddenly opened, an extremely intense pulse of short width (8 ns) is created.

With pulse width fixed (8 ns) and wavelength selected (1064 nm), the only adjustable variable is pulse energy. Energy per unit area of the beam is the fluence and commonly reported in mJ/cm<sup>2</sup>. The beam diameter is 9 mm and was not expanded or focused. The easiest way to vary pulse energy is to simply change the flash lamp pumping voltage on the laser controller. However, in doing so the experimental timing is altered because the delay between triggering the laser pulse and actual pulse is on the order of tens to hundreds of ns. This delay increases with decreasing lamp voltage. More importantly the timing stability worsens with decreasing lamp voltage. For instance, the delay variability at 125 mJ/cm<sup>2</sup> or 1.13 kV of pumping power is around 40 ns, an unacceptable timing fluctuation when trying to resolve Time-Temp-History (TTH) in five ns intervals. For this reason a fixed lamp voltage of 1.30 kV was used. The corresponding delay from trigger to laser pulse is 70 ns. The pulse jitter is less than two ns shot to shot. Additionally, pulse energy consistency is better at higher pumping voltages and the shot to shot pulse energy varied by less than 5%. As flash lamps age the stability declines, new flash lamps were installed at the beginning of this study and checked often for consistency. Laser fluence was varied by partial beam rejection with the use of partially reflective mirrors that were easily moved in and out of the optical path as desired. Fine tuning the fluence was achieved by passing the beam through a homemade variable attenuator, comprised of two quartz windows

mounted on counter-rotating plates. The opposite rotation of the two windows acted to walk the beam back into the beam path by applying an equal and opposite angle change to the refracted beam, as determined by Snell's law. The setup is capable of reducing fluence by approximately four percent via reflection at each air-quartz (or quartz-air) interface (four interfaces, two from each window). The plane polarized light of the laser can be completely transmitted through the windows by utilizing the Brewster angle as found based on index of refraction.

$$\theta = tan^{-1} {\binom{n_2}{n_1}} = tan^{-1} {\binom{1.4}{1}} = 54.5^{\circ}$$
 [3-2]

When plane polarized light propagating through air is incident upon quartz (index of refraction = 1.4) all of the light can will be transmitted if incident at  $54.5^{\circ}$ . By varying the angles of the windows, the intensity reduction via reflection at each interface can be varied from zero to four percent and can be calculated with the following equation:

$$R = \left(\frac{\left(\varepsilon_{2 \times \cos(\theta_{1}) \times \sin(\theta_{2}) - \varepsilon_{1 \times \sin(\theta_{1}) \times \cos(\theta_{2})}\right)}{\left(\varepsilon_{2 \times \cos(\theta_{1}) \times \sin(\theta_{2}) + \varepsilon_{1 \times \sin(\theta_{1}) \times \cos(\theta_{2})}\right)}\right)^{2} [3-3]$$

Equation 3-3 gives the relative reflective loss at the first air-quartz interface and this value is the same at the exiting quartz-air interface and at the interfaces in the second window. Where  $\varepsilon_1$  is permittivity of air,  $\varepsilon_2$  is permittivity of quartz,  $\theta_1$  is incident angle (set by user), and  $\theta_2$  is the angle of refracted beam through the quartz window. The refracted beam angle is simply calculated with Snell's law:

$$n_1 \sin(\theta_1) = n_2 \sin(\theta_2) \tag{3-4}$$

The optical path is illustrated in Figure 3-3.



Figure 3-3. Nd:YAG laser beam path.

Upon exiting the laser, the beam is first passed through a homemade variable attenuator comprised of two quartz windows mounted on counter-rotating plates. The quartz windows are housed inside of a black box that acts as a beam dump for the reflected rays. After

exiting the second quartz window the beam travels to a lens with maximum reflection for 1064 nm and maximum transmission for wavelengths between 300 and 625. Although the harmonic generator is switched out, some residual 532 nm laser light is produced and transmitted into a beam dump, the 1064 nm laser light is steered upwards where it meets a mirror that directs it to the right. Up to three partial reflectors are moved in and out of the optical path to limit fluence, the reflected beams are sent off to a beam dump. The beam is then again filtered to remove any remaining 532 nm light prior to striking a mirror directing the beam downwards and towards the sample. Prior to striking the sample the wings of the beam are clipped off by a five mm aperture. Following the aperture a ground glass diffuser is used to convert the Gaussian beam into a top-hat-like beam prior to heating the sample. The cavity design of pulsed Nd:YAG lasers are designed to be geometrically unstable. Theses cavities generate a spatial profile that varies throughout the pulse.<sup>130,131</sup> The temporal-spatial variation increases with decreasing lamp voltage, an additional benefit of adjusting fluence via beam rejection rather than lamp voltage. The transverse-modes of the Gaussian beam produced due to the temporal-spatial variations can result in non-uniform sample heating. To combat this the wings of the Gaussian beam are clipped off and only the center most 5 mm is used and when heating a TEM grid directly, only the center most 3 mm are used (diameter of TEM grid). Additionally, a ground glass diffuser is used to provide uniform illumination of the sample by forming a top-hat-like beam. Burn patterns with and without passage through the diffuser are shown in Figure 3-4.



Figure 3-4. Burn pattern of 9 mm Nd:YAG pulse without (left) and with (right) translation through a ground glass diffuser.

After translation through the ground glass diffuser the beam is directed into the sample chamber. An image of the sample chamber is shown in Figure 3-5. The beam is transmitted through a quartz window and strikes the sample. The sample is typically heated directly on 300 mesh-copper lacey carbon TEM grids. The grids are held in a steel sample holder with recessed holes as can been seen in Figure 3-5. The sample holder slides in the chamber and makes a vacuum tight seal with Del-Sealed<sup>TM</sup> copper washers. The sample holder can hold six grids at a time and is in translatable and rotatable from the exterior of the chamber.



Figure 3-5. Nd:YAG sample chamber.

Vacuum heating is performed at pressures below 100 millitorr by pulling vacuum with a vacuum pump and measuring pressure with a Baratron® capacitance manometer. Additional plumbing is used to introduce gas environments. The LII signal is detected through the quartz window and the detection systems are calibrated through the same window. Pulse energy was measured with an Ophir Nova energy meter, attached to an Ophir model 30(150)A-HE-DIF-17 head.

### 3.3.2 CO<sub>2</sub> Laser

A 250 Watt Synrad Firestar series F201 continuous wave CO<sub>2</sub> laser was used for laser heating of carbon materials. CO<sub>2</sub> lasers have a gas mixture of approximately 0.8/1/7CO<sub>2</sub>/N<sub>2</sub>/He. The CO<sub>2</sub> molecules are the active lasing medium. Nitrogen is used to provide collisional excitation of the vibrational energy states of CO<sub>2</sub> molecules and helium provides good conduction and stabilization of the plasma that is formed when the laser is pumped with 40.68 MHz radio frequency (RF). The success of the CO<sub>2</sub> laser is owed to a quirk of nature, diatomic nitrogen oscillates in a singular way and has exactly the energy required to pump ground state CO<sub>2</sub> to the upper laser level (001 asymmetric stretch) upon collision. An energy diagram of the process and the vibrational modes of CO<sub>2</sub> are given in Figure 3-6.



Figure 3-6. CO<sub>2</sub> laser energy level diagram and vibrational modes.<sup>95</sup>

The lifetime of excited nitrogen is long and thus efficiency of the CO<sub>2</sub> laser is high (15–20 %).<sup>95</sup> The predominant laser light emitted from a CO<sub>2</sub> laser is 10.6 µm from the transitions of (001)  $\rightarrow$  (100) (asymmetric to symmetric). Some 9.6 µm from (001)  $\rightarrow$  (020) (asymmetric to double bending) is also produced at much lower rates.

The laser was made to pulse by turning on and off the RF pump, controlled with a DG 535 pulse generator. The shortest obtainable pulse width is 100 microseconds ( $\mu$ s) due to the rise and fall time of the lasing medium. The power of the laser beam can be controlled via pulse width modulation. Pulse width modulation varies the duty cycle of the RF amplifiers, which in turn controls time averaged power. Rapid cycling the RF signal (faster than rise and fall times of the laser medium) acts to reduce power and maintain a true continuous wave laser beam. The output beam is of very high spatial and temporal quality. The delay between trigger and pulse is a constant 100  $\mu$ s. The output beam diameter is 4 mm. A Galilean beam expander was used to increase the beam diameter to 12 mm. The beam expander assembly was easily moved in and out of the optical path depending on desired intensity (i.e. temperature). The optical path is shown in Figure 3-7.



Figure 3-7. CO<sub>2</sub> laser beam path.

Upon exiting the laser the beam was directed upwards with a silver turning mirror, silver mirrors were selected due to their high reflectivity for  $CO_2$  laser light and high damage threshold. A second turning mirror directed the beam though an optional Galilean beam expander. The beam expander is comprised of two ZnSe anti-reflective coated lens: a 0.75 inch plano-concave lens with a focal length of negative 1 inch and a 1.5 inch plano-convex lens with a focal length of 3 inches. The lenses are separated by the sum of their focal lengths (2 inches). Since the plano-concave lens has a negative focal length, the separation distance is shorter than it would be in a Keplerian design and is advantageous when working in tight spaces. Additionally, the Galilean beam expander does not focus the light to a point between the lenses as done in a Keplerian design and thus avoids wavefront errors and the danger of an extremely intense focused laser beam capable of producing an electric arc in air. The incident light is divergent upon exiting the plano-concave lens and is collimated by the plano-convex lens. The beam magnification is equal to the absolute value of the ratio of focal lengths:

$$Magnification = \left| \frac{f_{objective \,lens}}{f_{image \,lens}} \right| = \left| \frac{3}{-1} \right| = 3$$

$$[3-5]$$

After exiting the beam expander the beam is directed down towards the sample with an additional turning mirror. Prior to striking the sample the beam is passed through a ZnSe diffuser to convert the Gaussian beam to a top-hat-like beam for the purpose of uniform sample heating. The ZnSe diffuser was made in house since they are not commercially available by sanding one side of ZnSe window with 600 grit sand paper. The CO<sub>2</sub> sample chamber is identical to the previously illustrated Nd:YAG sample chamber except that the laser input window is ZnSe, not quartz.

Due to the longer pulse durations used during  $CO_2$  laser annealing (hundreds of  $\mu$ s to several minutes) as compared to Nd:YAG laser annealing (8 ns). Direct heating on TEM grids was not possible as the grids were completely melted/vaporized. For this reason the TEM grid sample holder was not used and also because the steel holder reflects most of

the beam and results in burning of the O-rings in the sample chamber and stray rays exiting out the ZnSe window with high intensity. A graphite beam dump was used to absorb the beam and eliminate reflection. A Plexiglas cage was built around the sample chamber to catch any possible reflected laser radiation. Samples were heated in thin powder form and held in a graphite block with a 3 mm wide and 2 mm deep hole. Samples were directly heated on TEM grids when annealing with the beam expander in as beam expansion lowers intensity (i.e. temperature) and the TEM grids survive. Pulse energy was measured with an Ophir Nova energy meter, attached to an Ophir model FL250A-BB-35 fan cooled head.

## 3.3.3 Laser Induced Incandescence Signal Detection

One of the most important measurements in this study is the Time-Temperature-History (TTH). A TTH provides much more insight into the process of thermal annealing than does a simple HTT, as has been the metric used to date. Laser annealing provides rapid heating. Cooling is also rapid due to controlled local heating. How fast and how hot are determined by measuring the Laser Induced Incandescence (LII) signal. The measurements made in this study have ns temporal resolution and absolute temperature resolution within a couple-few tens of °C, as will be demonstrated here.

The instrumentation used to measure the LII signal includes: a 500 MHz Tektronix<sup>®</sup> digitizing phosphor oscilloscope, a 200 MHz Tektronix<sup>®</sup> digitizing phosphor oscilloscope, high speed silicon and germanium photodiodes, free standing and spectrograph mounted nine stage Hamamatsu R636-10 Photomultiplier Tubes (PMTs)-fitted in Acton Research Corporation housings (model PD439), spectrographs/monochromators - 1/4 meter SpectraPro<sup>®</sup>-275 with PMT attachment and a 0.3 meter Princeton Instruments Acton SP2300<sup>®</sup> with ICCD attachment, a Princeton Instruments PI-Max® gated Intensified Charge Coupled Device (ICCD), a Princeton Instruments controller (model ST-133), Stanford Research Systems four channel digital delay/pulse generators (model DG 535), band pass filters, and WinSpec-32 spectra collection software.

### **3.3.3.1 LII Detection System Calibrations**

The spectrograph-camera system was calibrated using a Hg-Ar calibration lamp, with known elemental emission wavelengths within in the UV and near-IR range. The calibration light source is an Ocean optics<sup>®</sup> Cal-2000 Hg-Ar lamp. The observed wavelengths were then assigned to specific camera pixels that served as points of known wavelength. A non-linear curve-fit through these point's serves to define wavelengths across the detector array. The pixel assignment of known spectral lines from the Hg-Ar lamp is illustrated in Figure 3-8.



Figure 3-8. Hg-Ar wavelength calibration.

The second spectral calibration pertains to the correction of observed intensities. Both the ICCD and PMTs were calibrated with an Optronic Laboratories black body tungsten lamp (HTS-94) light source. The HTS-94 spectral output is continuous, originating from a Joule-heated tungsten filament. When a steady eight amp current is supplied, the HTS-94 lamp emits known spectral irradiance ( $\mu$ W/cm2). The PMT response compared to known HTS-94 signal is shown in Figure 3-9.



Figure 3-9. Photomultiplier tube response curve to HTS-94 calibration.

Each PMT response data point is from an indivudial measurement, unlike an ICCD a PMT does not differentiate wavelenghs. The PMTs used here are preceeded by a monochromator or band pass filters to resolve wavelength. From the above graph, wavelength dependent intesity correction factors are found, a few of which are displayed in Table 3-1 for illustration.

Table 3-1. Photomultiplier tube wavelength dependent intensity calibration.

lambda	correction					
	factor					
400	0.178067					
550	1.028829					
750	2.095031					

The ICCD was wavelenght intensity calibrated for each spectrograph grating and grating postion. Response curves from a 150 grove/mm grating at various postions are shown in Figure 3-10.



Figure 3-10. ICCD wavelength intensity response curves.

As seen in Figures 3 - 9 and 10, both the PMT and the ICCD have good broad spectral response, with detection spanning the UV to near-IR. Each spectra (A/B/C) in Figure 3-10 is from a single collection using the full chip (256 X 1024 pixel). The camera (ICCD) is rotated so that the wavelength axis is 1024 pixels wide and each pixel is approximately 0.5 nm wide when using the 150 grove/mm low resolution grating. Each pixel is assigned an intensity calibration correction factor. Higher resolution gratings employ a much higher pixel/nm ratio, but observe a more limited wavelength range. For the purpose of fitting LII signal to Planck's black body distribution for temperature fitting via multi-wavelength pyrometry, a wide wavelength range is desired. Additionally, the grating efficiency is better for lower resolution gratings, more incident light will reach the detector.

#### 3.3.3.2 Pyrometry

The carbon materials used in this study can be well approximated as black body absorbers, as evident by good LII signal fit to Planck's black body radiation curves. Absolute temperature is found by fitting measured and corrected LII spectra to black body radiation curves found with Planck's equation:

$$B_{\lambda} = ({}^{2} \times h \times c^{2} / {}_{\lambda^{5}}) \times (e^{hv/K_{B}T} - 1)^{-1}$$
[3-6]

Where  $B_{\lambda}$  is spectral intensity per unit wavelength, *h* is Planck's constant, *c* is the speed of light,  $\lambda$  is wavelength, *v* is frequency,  $K_B$  is the Boltzmann constant, and *T* is absolute temperature.

Both the PMT and the ICCD can be used to find temperature. The LII signal is delivered to the detection systems through a multi-bundle fiber optic cable. With the PMT, only a few wavelengths are utilized and thus this approach is termed few-wavelength pyrometry. The spectra collected with the ICCD contains hundreds of wavelengths and is referred to as multi-wavelength pyrometry. A comparison on the two approaches follows. In a photomultiplier tube incident photons pass through a quartz window and strike a photocathode and in return the photocathode releases electrons. Thereafter it is the electrons that are multiplied. The electrons are directed towards the electron multipliers (dynodes) by a focusing electrode. The electrons are impacted on dynodes that produce more electrons in the process, each dynode is held at a higher driving voltage than the preceding one. Driving voltages used in this study ranged from 800 to 1100 Volts. After amplification at all the dynodes, current flows from the anode and is measured directly with a digital oscilloscope. The intensity is directly proportional to the incident photon intensity. An illustration of PMT operation is provided in Figure 3-11.



Figure 3-11. Photomultiplier tube operation.

A schematic of the major components of an ICCD are displayed in Figure 3-12. Like the PMT incident photons strike a photocathode and in return the photocathode releases electrons. These electrons are then multiplied by passing through a microchannel plate, as the electrons hit the channel walls additional electrons are generated. The gain used to accelerate the electrons through the microchannel plate is user controlled. Upon exiting the channels, electrons are further accelerated by an 8 kV voltage before striking a phosphor coating. The phosphor coating acts to convert the electrons into photons, at this point there are now many more photons for each original incident photon that struck the photocathode. The photons are transferred to the CCD via fiber optic coupling. Every pixel is fiber optically coupled. Charge then accumulates in the pixel well until the microchannel plate is gated off. The accumulated charge is then digitized and transferred to the host computer.



Figure 3-12. Schematic of the major components of an ICCD.<sup>132</sup>

Gating on and off via a voltage bias acts as a virtual shutter. In Figure 3-12 the ICCD is gated on because the photocathode is biased more negative than the microchannel plate and therefore the CCD will be exposed. When biased off (gated off) the photocathode is biased to positive 200 V and no photons make it to the CCD. The PI-MAX camera system was controlled with an ST-133 controller capable of biasing on and off the camera in as short as 2 ns. By stepping out the gate delay and collecting LII spectra from short gate

widths, detailed TTHs can be obtained.

A comparison of a TTH collected from the PI-MAX camera system to the time trace collected from a PMT are provided in Figure 3-13. The LII signal was collected from a carbon black powder bed heated with a 200 mJ/cm<sup>2</sup> Nd:YAG laser pulse under an argon atmosphere. Time traces from the PMT were collected using select 10 nm wide wavelength bandpass filters. The PMT is potentially advantageous because it measures signal in real time, the spectral intensity as a function of time is read out with a digital oscilloscope. As seen in Figure 3-13C, the PMT time traces have ns temporal resolution. Therefore, relative wavelength intensities can be used to extract a temperature with ns resolution. However, temperatures found in this way are in error as they were found to randomly increase and decrease with large fluctuations. This is likely limited by a poor signal to noise ratio. To improve the signal to noise ratio, temperatures were found by averaging the intensities in 10 ns intervals and again were found to be nonsensical. Using the peak wavelength intensities occurring at 15 ns as displayed in Figure 3-13C, the extracted temperature is ~ 3,900 °C. The inferred time above temperature from the PMT time traces suggest that the material has cooled to a temperature low enough not to emit measureable incandescence after 70 ns. However, the camera system recorded elevated temperatures above 2,000 °C 1.5 µs after the laser pulse, Figure 3-13B. Figure 3-13A shows the first 100 ns TTH recorded with the camera system. Figure 3-13B shows the cooling profile after the first 100 ns. Clearly there is large disagreement between the cooling times observed from the PMT and the ICCD. To reconcile this the entire LII signal (i.e. no preceding bandpass filter) was sent to the PMT. The observed time trace was approximately 3 microseconds, in good agreement with the camera system. Therefore, the PMT is signal limited when bandpass filters or a monochromator proceeds the detector. Therefore, the TTHs obtained from the camera system are far superior. The PI-MAX camera system has far greater dynamic range than that of the PMT and has the widest dynamic range of any ICCD camera in the market today.<sup>132</sup> The ~ 3,900 °C measured from the maximum intensity PMT signal is in agreement with the maximum temperature found using the camera system.



Figure 3-13. Time-temperature-history recorded with PI-MAX camera system (A and B) and time traces collected from a PMT (C).

To verify the timing of the camera system, the residual 532 nm laser light emitted from the Nd:YAG was scattered off of a steel sheet and detected. This light is typically sent to a beam dump as was shown previously in Figure 3-3. The pulse width of 532 nm laser light is  $\sim 8$  ns long. The camera was set for prompt detection at the start of the laser pulse with a gate width of 2 ns. The 532 nm laser light was observed. A second time check delayed detection 2 ns after extinction of the laser pulse, or a 10 ns delay from the start of the pulse with a width of 2ns. Very low 532 nm signal was detected at a 10 ns delay and this was expected as the 8 ns laser pulse width is a full width half maximum time value. With an additional 2 ns delay (i.e. 12 ns) no signal was detected. Detected signal at the start of the pulse and 10 ns after the start of pulse with collection durations of 2 ns are shown in Figure 3-14.



Figure 3-14. Prompt 532 nm laser scatter detection (A) and delayed detection (B).

## 3.3.3.3 Nd:YAG Laser LII Signal Detection

A 500 MHz Tektronix<sup>®</sup> digitizing phosphor oscilloscope was used to determine the experimental timing involved in Nd:YAG laser annealing. The master trigger was the "sync-out" signal provided from the laser controller. The delay between trigger signal from the laser and LII signal was determined using a fast response (less than 2 ns) germanium photodiode. The initial delay time was fixed for all experiments because the laser was operated at a fixed lamp voltage setting, see section 3.3.1. The delay between trigger and observed LII signal is 70 ns as displayed in the oscilloscope display in Figure 3-15. Also shown is the camera monitor. The gate delay and gate width of the camera system were monitored on the oscilloscope during collection of TTHs.



Figure 3-15. Nd:YAG experimental timing.

The shortest possible camera gate width is 2 ns. The TTHs collected in this study typically measure the first 2 ns of LII signal, see first data point in Figure 3-13A. The first 2 ns integrated average temperature is  $3,330 \text{ °C} \pm 30 \text{ °C}$  from a carbon black powder bed heated with a 200 mJ/cm<sup>2</sup> Nd:YAG laser pulse. The samples continue to increase in temperature with the 8 ns laser pulse before rapidly cooling. The gate delays and gate widths used to monitor the LII signal from Nd:YAG laser heating are provided in Table 3-2.

Gate Width [ns]	Gate Delay from LII Signal [ns]				
2	0				
5	0-45 in 5 ns increments				
25	50 and 75				
100	100 - 900 in 100 ns increments				
500	1,000 - extinction in 500 ns increments				

Table 3-2. Nd:YAG LII signal collection times.

As cooling rate slows gate delays are stepped out in larger increments and longer gate widths are required in order to acquire adequate signal levels. Each data point in Figures 3-13 A and B were collected 3 times and standard deviation about the mean is less than 40 °C. The ST-133 programmable pulse generated was used to control the camera gate delay and width.

## 3.3.3.4 CO<sub>2</sub> Laser LII Signal Detection

Pulse widths of 100  $\mu$ s to 5 minutes were used during CO<sub>2</sub> laser heating experiments. These time scales are incompatible with the ST-133 programmable pulse generator, used to control the camera during Nd:YAG laser heating experiments. A four channel DG 535 pulse generator was used to control experimental timing in conjunction with the host computer and WinSpec software during CO<sub>2</sub> laser heating. Channel-A of the pulse generator was used to trigger the laser, channel-B was used to define laser pulse width, and channel-C acted as the external trigger for controlling the camera gate delay. The camera gate width was set in WinSpec under shutter mode timing control. The camera gate delay signal is delayed off of channel-A, the laser trigger.

LII signal is delayed 100  $\mu$ s from the trigger due to the rise time of the lasing medium. The earliest detected temperatures collected from the first few  $\mu$ s of LII signal are approximately 1,600 °C and temperature increases to a maximum of 2,600 °C gradually over a duration of 1.4 ms. This maximum temperature is constant for the duration of the remaining laser pulse. Cooling is dependent upon quantity of heated sample, cooling times are on the order of tens of ms. Samples follow a similar heating and cooling trend when the beam expander is in, but maximum temperature is limited to approximately 1,700 °C.

#### 3.3.4 Black Body Fitting & Semi-Automation

Temperatures were found by using the black body approximation. The validity of a black body approximation is determined by the fit. When observed over a wide range of wavelengths, this approximation appears valid as suggested by black-body fits to experimental data shown in Figure 3-16. In particular, the same temperature is found using all of the detectable wavelength range. The three spectra were acquired from the same heating conditions and camera timing, but at different positions of the spectrograph grating.



Figure 3-16. Black-body fits across entire detectable wavelength range.

A dependence of emissivity on wavelength would manifest itself as discrepancies in the Planck black-body fit across the 275 - 850 nm wavelength stretch, showing different temperatures for different regions of the spectra. Since this is not observed the black-body approximation is valid.

The black body temperature fitting was semi-automated with a macro written in Microsoft Excel. Each data point of the input spectra was multiplied by the wavelength dependent intensity correction factor, after intensity correction the input spectra was normalized, temperature was then determined based off a least squared fit from a database of precalculated and normalized black body intensity values over the same wavelength range. The databased includes temperatures spanning from 800 °C to 4,600 °C in 25 °C increments. A selection of the macro is displayed in Figure 3-17.

Lambda	Normalized Spectra					Lambda	2350 K	R_Squared	2375 K	R_Squared
500.001	0.000983511		Paste Wavelength Range			500.001	0.000803	9.51E-06	0.000855	1.11E-05
500.554	0.001036083					500.554	0.000809		0.000861	
501.106	0.001008032					501.106	0.000816		0.000868	
501.659	0.001014532		Refrech Sheet			501.659	0.000822		0.000875	
502.211	0.001042072		ne	ilesii sheet		502.211	0.000829		0.000882	
502.764	0.001011807					502.764	0.000836		0.000888	
503.316	0.001046093			Clear R^2		503.316	0.000842		0.000895	
503.869	0.001026468					503.869	0.000849		0.000902	
504.421	0.001044145	Average	0.003476			504.421	0.000855		0.000909	
504.974	0.00105345					504.974	0.000862		0.000916	
505.526	0.001035868					505.526	0.000869		0.000923	
506.078	0.001101736					506.078	0.000876		0.00093	
506.631	0.001059073			Min	9.509083E-06	506.631	0.000883		0.000936	
507.183	0.001046978			Temperature	2350 K	507.183	0.000889		0.000943	
507.735	0.001061704					507.735	0.000896		0.000951	
508.288	0.001057187		Calculate Best Fit			508.288	0.000903		0.000958	
508.84	0.001078708					508.84	0.00091		0.000965	

Figure 3-17. Semi-automated black body temperature fitting Microsoft Excel macro.

# 3.4 Material Characterization

The extent of material transformation upon traditional and laser annealing was characterized with XRD, TEM and various techniques used in the transmission electron microscope. The carbon lamellae (La) and crystallite stacking (Lc) growth, and lattice spacing ( $d_{002}$ ) were measured by XRD. Bright field HRTEM images were processed with in-house image analysis codes to provide complimentary measurements of La and Lc, with direct visualization. Lamellae planarity or de-wrinkling is measured by a decrease in fringe tortuosity, a metric extracted form HRTEM image analysis. The alignment of lamellae into the graphite lattice is measured by the  $d_{002}$  spacing from both X-ray and electron diffraction techniques. Growth, stacking, and alignment are all measures of the physical changes occurring during annealing. The chemical change accompanying annealing is the conversion of sp<sup>3</sup> hybridized carbon to sp<sup>2</sup> hybridized carbon and was measured with Electron Energy Loss Spectroscopy (EELS) in the TEM.

Carbonization products prepared in sealed tubing reactors were characterized with polarized light microscopy to measure the extent of mesophase development that occurred during carbonization.

# 3.4.1 Reflected Polarized Light Microscopy

Two polarizing filters are used in a polarized-light microscope: the polarizer located between the light source and sample and the polarizer between the detector and the sample. The polarizers are arranged perpendicular to one another, such an arrangement is known as cross-polarization or cross-polars. For light to reach the detector the sample must change the polarization of incident light. When the sample is isotropic (i.e. properties are the same in all directions) there is no change in polarization and light does not reach the detector.<sup>133</sup> An optically anisotropic sample is birefringent, with directional dependent index of refraction values. Birefringent materials generate an ordinary ray that remains plane

polarized and an extra ordinary ray that is perpendicularly polarized (s polarized). Therefore, light from optically anisotropic samples reaches the detector.<sup>133</sup> The use of a retardation plate that removes green light from the white light source results in primary and secondary coloration that helps define optical texture.<sup>134</sup> For non-graphitic carbons with a built in flow direction of BSUs formed during mesophase, the observed colors are typically purple, blue, and yellow.<sup>135</sup> Yellows and blues result from the prismatic edges of exposed BSUs. Upon stage rotation of 180° the blue regions turn yellow and the yellow regions turn blue. Purples results from the two light components traveling and reaching the detector at the same time. These regions correspond to the basal planes lying parallel to the polished surface and do not change color upon stage rotation.<sup>135</sup> Isotropic regions do not change color upon stage rotation.

Polarized light microscopy was employed to measure the extent of mesophase development from carbons prepared in sealed tubing reactors. A highly polished surface is required to view the microstructure at the focal length of the microscope.<sup>134</sup> In order to increase the mechanical integrity needed to hold the carbon in place during polishing, carbon materials were set in epoxy. Polishing was carried out in several stages, the carbon samples mounted in epoxy were held with a pellet holder (Leco VP-160, Leco Inc.) and sanded down using a series of 240, 400, and 600 grit sand disk papers. A polishing wheel was used at 300 rpm for 3 minutes during each polishing stage. Polishing was then followed by a series of alumina polishing slurries (0.3 and 0.005 mm particle size) dispersed onto cloth surfaces.

A Nikon Microphot-FXAII microscope was used to collect surface images at magnifications between 5 and 100 and scanned the entire surface. Select samples were imaged with a Zeiss Universal research microscope at a magnification of 625 with an oil immersion lens.

### **3.4.2 X-Ray Diffraction**

X-ray diffraction patterns were collected with a PANalytical Empryean X-Ray Diffractometer using  $K_{\alpha}$  copper radiation (1.54 Å). Samples were analyzed in powder form and crushed with a mortar and pestle. Samples were scanned from 15-90 degrees 2- $\theta$ . To correct for instrument broadening, an external standard (silicon) was measured and then the sample. Instrumental broadening, background removal, peak fitting, and analysis were performed using JADE<sup>®</sup> XRD software. The d<sub>002</sub> layer plane spacing was found using the Bragg equation:

$$n\lambda = 2dsin(\theta)$$
[3-7]

Where  $\lambda$  is the X-ray beam wavelength, the angle of diffraction is 2 $\theta$ , and the layer plane spacing is d, and n is the order of diffraction. The (002) planes are first order. This spacing was compared to the second order (004) values as a complementary measure when

sufficient crystallinity was present to give rise to a well-defined (004) peak. Crystallite stack height (Lc) and layer diameter (La) were found by the applying the Scherrer equation:

$$L_{a/c} = \frac{K\lambda}{\beta cos(\theta)}$$
[3-8]

Where K is a dimensionless shape factor equal to 0.89 for La and 1.84 for Lc,  $\lambda$  is X-ray wavelength,  $\beta$  is the line broadening at full width half maximum measured in radians, and  $\theta$  is the angle. La was taken from the (110) peak found at 77° when adequate signal was available. La values from the (100) peak at 42° are not resolved from the (101) peak at 44° from disorganized carbons. Although, for completely disorganized carbon there should be no 3-dimensional crystal and thus (101) should not be present. In practice, the broadening of the (100) due to layer stacking is present in disorganized carbons and the (110) is therefore a more appropriate peak to use for La. The Lc value was taken from both the (002) and (004) peaks.

#### 3.4.3 Transmission Electron Microscopy

High Resolution Transmission Electron Microscopy (HRTEM) was used for direct visualization of nanostructure before and after annealing. Microscopy was performed on a FEI Talos. Nanostructure (lamellae observed as (002) fringes) was observed in bright field mode at magnifications of 500,000 and 630,000. To aid in interpreting the 3-dimensiallity buried in the 2-dimensional projection, samples were tilted to both positive and negative angles. If the carbon basal planes are perpendicular to the electron beam they will be transparent as they will not satisfy the conditions for diffraction. Phase contrast HRTEM images are interference patterns of the direct and diffracted beam(s). In a few cases tomograms were created by acquiring a tilt series of images tilted to +/- 70 degrees in one degree increments. Reconstruction of the 2-dimensional images into a 3-dimensional representation was performed using Avizo software.

High Angel Annular Dark Field (HAADF) images were collected in Scanning TEM mode (STEM) and used for identifying thickness. HAADF images are produced from Rutherford backscattered electrons and thus the brightness in the HAADF images is a function of both atomic composition (Z-contrast) and thickness. In nearly pure carbon samples the contrast is thickness related.

A simplified ray diagram (i.e. electron trajectories) from sample to image is displayed in Figure 3-18. The electron source is above the sample in this illustration and the angles are highly exaggerated for the purpose of illustration. The electrons traverse through a thin sample either directly or diffract if the conditions (i.e. parallel alignment of crystalline planes) for Bragg diffraction are satisfied. The transmitted electrons contain the crystalline information with high spatial resolution. The electron are then focused by an objective lens to the back focal plane. The lenses in an electron microscopes are electro-magnets. A diffraction pattern is created at the back focal plane. Parallel rays transmitted from the sample carry the same lattice spacing information and can be traced to the same spot in the

back focal plane (diffraction pattern). An objective aperture is inserted into the back focal plane for the purpose of selecting the diffracted beams to be used in the phase contrast image. In practice a 70  $\mu$ m objective aperture will result in use of only the direct and (002) diffracted beams in the phase contrast image. The observed images are (002) fringes.



Figure 3-18. Ray diagram for a transmission electron microscope.<sup>136</sup>

The diffraction pattern is in inverse space and therefore by inserting larger objective apertures into the back focal plane diffracted beams carrying shorter spatial information are including in the image. A 70  $\mu$ m aperture was used to collect HRTEM images in this study. There exists a tradeoff between resolution and contrast and is controlled with objective aperture selection. For the purpose of image processing via computer codes, high contrast is desired.

As mentioned the lenses are not physical, but rather electromagnetic. Therefore, they limit resolution by inducing spherical aberration because the focusing strength is not uniform. Electrons passing though the objective lens will be focused with decreasing strength the further they are away from the electromagnetic lens. This results in multiple focal lengths and turns a point in the object into a disk in the image. Spherical aberration is the main resolution limiting factor. Advanced microscopes can remove this aberration via spherical aberration correction that acts to apply a bias from an octagonal magnetic lens under the objective lens. The FEI Titan is equipped with dual spherical aberration correctors and can provide true atomic resolution. However, to resolve atomic resolution the sample must be single layer or a perfectly flat couple layers. No objective aperture is used when the aberration corrector is activated.

Care must be taken in the interpretation of HRTEM images. The image contains 3dimensional information in 2-dimensions. Consider the two headed beast in Figure 3-19. Common sense tells us that this is an optical illusion. Our eyes are well suited to question the existence of this two headed rhino, as our vision relies mainly on reflection imaging. However, our eyes are ill suited to distinguish a multiple projection in a transmission image.



Figure 3-19. Two headed rhino.<sup>136</sup>

For instance, a sample may appear as a multiwall nano-onion like particle or as a hollow particle simply by tilting the sample, see the HRTEM micrographs in Figure 5-24. A multiwall CNT oriented endcap up will appear as a multiwall circle in the image as the (002) planes in the end cap would be closer to perpendicular than parallel to the beam and would not satisfy the condition for Bragg diffraction. Angle tilting is used to ascertain the true structure observed in HRTEM images.

# 3.4.4 Image Processing

HRTEM images were processed with in-house Matlab codes for the purpose of extracting La, tortuosity, and number of lamellae per stack. The Fringe Analysis code developed by Kuen Yehliu is used to extract the distributions of La and tortuosity.<sup>137</sup> Previous studies by Vander Wal et al.<sup>138</sup>, Yehliu<sup>137</sup>, Hung<sup>88</sup>, and Gaddam<sup>123</sup> have all shown the applicability of

this code for soot and have demonstrated that is statistically meaningful. Although the image processing involves several operations, it is simplistically represented in Figure 3-20.



Figure 3-20. Fringe analysis illustration.

As seen in Figure 3-20 the input HRTEM image is skeletonized and the distribution of La and tortuosity are extracted from the skeletonized image. The stacking code developed by Enette Louw<sup>139</sup>, skeletonizes a HRTEM micrograph and calculates the number of carbon lamellae per stack based on three user defined parameters: the maximum allowed spacing between two layers, the angle between the layers, and the centroid to centroid distance of the layers. Values of 3.8 Å, 10°, and 8 Å were selected as the three controlling parameters. An illustration of the Stacking code is provided in Figure 3-21.



Figure 3-21. Illustration of the Stacking code.

### **3.4.5 Selected Area Electron Diffraction**

Selected Area Electron Diffraction (SAED) patterns were collected on the FEI Talos transmission electron microscope. The SAED patterns compliment the XRD measurements. Where XRD provides bulk material average data, SAED can collect diffraction patterns from nm sized regions of interest. Laser annealing generates small sample quantities, directly on TEM grids in the case of Nd:YAG laser annealing, below the required ~ 50 mg needed for XRD. Thus, SAED was used to ascertain the  $d_{002}$  layer plane spacing of laser annealed samples. The (002) diffraction ring is a convolution of diffraction functions. The true or weighted spacing average is found by measuring the distance between peak intensity. Image-J software was used to ascertain this distance, as it is not readily determined by eye and not measured preciously by hand.

### **3.4.6 Elemental Analysis**

Energy Dispersive X-Ray Spectroscopy (EDS) was performed on the FEI Talos transmission electron microscope in STEM mode for the purpose of elemental analysis. When an incident electron collides with a core shell (K) electron the core electron is ejected, leaving behind a core hole in its place. An electron from an outer, higher-energy shell rapidly drops down to fill the core hole. Most commonly an L shell electron will drop down to fill the void in the K shell. When this happens the higher energy L shell electron sheds excess energy in the form of a characteristic X-Ray. This X-ray is unique to the element from which it was emitted. The characteristic X-ray is detected with silicon drift detectors. The Talos is equipped with a Super-X EDS system that is comprised of four silicon drift detectors. Using multiple detectors increases the signal to noise ratio and allows for identification of light elements. Elements lighter than Beryllium with low fluorescence-yield (Li, He, H) are not detectable. In STEM mode EDS provides high spatial resolution. The resolution of EDS is limited to a few atomic % due to the background noise generated via Bremsstrahlung braking radiation.

Hydrogen content was measured using a CHN analyzer manufactured by LECO Corporation. Samples were burned in a pure oxygen stream and IR detectors measured hydrogen content in the form of H<sub>2</sub>O. Approximately 45 mg of sample was required for analysis. Standard samples of similar composition were used as calibration standards. In a similar fashion sulfur was measured using a sulfur–carbon analyzer (Model SC144-DR LECO Corporation).

## **3.4.7 Electron Energy Loss Spectroscopy**

Electron Energy Loss Spectroscopy (EELS) was used to measure carbon hybridization  $(sp^2/sp^3)$ . High energy electrons from the beam loss energy (i.e. inelastically scatter) as they traverse through the specimen. An electron spectrometer separates electrons into a spectrum based on energy loss. The directly transmitted electrons are found in the zero-

loss peak that is used to determine the energy spread of the beam in eV and defines the EELS resolution. When a core shell electron is displaced by an incident electron it can scatter only into an available state and the energy transition required to scatter the core shell electron is imparted on the incident electron. For carbon, the core shell electrons can scatter only to the unoccupied antibonding  $\sigma^*$  and  $\pi^*$  states. The transitions from 1s to  $\pi^*$ and 1s to  $\sigma^*$  are ~ 285 and 292 eV respectively. The intensities are proportional to the density of states ( $\sigma^*$  and  $\pi^*$ ) and can thus be used to calculate sp<sup>2</sup> and sp<sup>3</sup> content. The carbon core-loss envelope is approximated to be 20 eV wide from the start of the  $\pi^*$ edge.<sup>77,140,141</sup> Quantitative EELS spectra is a challenge and requires either advanced computer modeling or use of an appropriate standard sample.<sup>136,142</sup> Graphite has been used as a standard due to the known 100% sp<sup>2</sup> content and 1:3  $\pi^*:\sigma^*$  density of states.<sup>77</sup> However, graphite is not an appropriate standard sample due to orientation effects (i.e. scattering cross-sectional areas depend on orientation). When the basal planes are perpendicular to the beam, the p-orbitals have a smaller scattering angle as compared to when the basal planes are parallel to the beam (i.e. p-orbitals perpendicular to the beam). The carbon nanoonion (made from graphitization heat treatment of carbon black) was selected as the calibration standard because of the spherical geometry, thus it is free of orientation effects, and is assumed to be 100% sp<sup>2</sup> (i.e. 1:3  $\pi^*:\sigma^*$ ). Calibration against the carbon-nano-onion is most applicable for soot and carbon black as the standard and unknown have similar thickness and geometry and determined  $sp^2$  is unchanging with angle tilt for these samples. For cokes and chars  $sp^2$  was found vary by as much as 5% upon sample tilting.

Measurements were taken on FEI Titan and FEI Tecnai transmission electron microscopes. Both microscopes use a Gatan GIF Quantum<sup>®</sup> electron filter. The dual spherical aberration corrected Titan microscope is fitted with a monochromator. EELS resolution is determined by the full width at half maximum value of the zero loss peak. Without use of the monochromator the Titan EELS resolution is 0.9 eV and 0.1 eV when the monochromator is activated. The conventional thermionic emission Tecnai has an EELS resolution of 0.9 eV, the same as the Titan without use of the monochromator. Carbon hybridization measurements were found to be the same with and without use of the monochromator. Additionally, Tecnai and Titan EELS measurements were the same and therefore the higher energy resolution of the Titan was not required. The Titan was used for STEM EELS measurements because the focused STEM probe on the Titan is 0.7 Å, compared to ~10-50 Å on the Tecnai. STEM EELS has the advantage of providing high spatial resolution. However, STEM EELS was shown to be non-reproducible as a likely result of beam damage from the intense focused beam. To avoid beam damage EELS measurements were performed in TEM mode with an expanded beam (i.e. low dose rate). Spectra background removal, plural scattering removal, peak fitting and integration were performed with Gatan Digital Micrograph software.
# **Chapter 4**

# **Carbonization and Traditional Thermal Annealing of Cokes and Chars**

In this chapter several cokes are chars are prepared via carbonization and subsequently subjected to traditional graphitization heat treatment of 2,600 °C for a duration of one hour. Mesophase development during carbonization is necessary to produce a graphitizable carbon (i.e. a coke). Carbon chars on the other hand do not pass through a fluid mesophase during carbonization and are non-graphitizable. The non-graphitizability of chars is owed to cross-linking between the BSUs. To date the nature of the cross-links are not well understood. The two leading models: the Distorted Graphene Triad (DGT) and the fullerene related nanostructure are in disagreement. The DGT model contributes nongraphitizability to resilient oxygen groups that cause defect regions between boundaries of graphene segments. The fullerene related model assumes that odd membered rings, predominantly pentagonal, are present in the virgin char and are the root cause of nongraphitizability due to the induced curvature caused by their presence. In this chapter several cokes and chars are prepared by carbonization in sealed tubing reactors and subsequently subjected to traditional (i.e. furnace) graphitization heat treatment at 2,600 °C for a duration of one hour. An emphasis is placed on exploring the non-graphitizing behavior of chars. Anthracene and sucrose (table sugar) were selected as the model graphitizing and non-graphitizing compounds based on historical precedence. Polyfurfuryl alcohol (PFA) and anthanthrone were also selected as oxygen containing carbon precursors. Pentagonal ring containing fluorene was both carbonized pure and cocarbonized with anthracene to investigate the effect of pentagonal ring systems on carbonization and subsequent heat treatment. Anthracene was also co-carbonized with sucrose and dibenzothiophene (DBT). Sulfur containing anthracene-DBT coke is compared to a coke produced from a commercial fluid catalytic cracking decant oil (DO) with similar sulfur content to investigate the impact of sulfur during graphitization heat treatment of cokes.

Mesophase development was assessed by measuring the materials optical anisotropy with a polarized light microscope. The degree of annealing was measured with XRD and visualized with HRTEM.

# 4.1 Contrasting Anthracene and Sucrose Carbonization and Subsequent Graphitization Heat Treatment

Anthracene and sucrose were selected as representative model compounds used to produce a graphitizable carbon and a non-graphitizable carbon, respectively. Anthracene is a planar PAH comprised of hexagonal rings and free of heteroatoms, sucrose has a complex structure that is fully saturated and rich in the element oxygen. Chemical structures are provided in Figure 4-1.



Figure 4-1. Chemical structures of anthracene (A) and sucrose (B).

# 4.1.1 Virgin Anthracene Coke and Sucrose Char

The carbonized products of the two compounds are shown in the polarized light micrographs in Figure 4-2. Anthracene experienced an extended mesophase development upon carbonization as evident by the high optical anisotropy shown in the polarized light micrograph (Figure 4-2A). Sucrose carbonization proceeded without the development of a fluid phase as observed by the complete lack of anisotropy in the polarized light micrograph (Figure 4-2B). The isotropic sucrose char is a highly porous material as compared to the compact anthracene coke.



Figure 4-2. Polarized light micrographs of anthracene coke (A) and sucrose char (B).

The nanostructure of anthracene coke and sucrose char are shown in the HRTEM micrographs in Figure 4-3.



Figure 4-3. HRTEM micrographs of anthracene coke and sucrose char.

Reconciling observations between polarized light microscopy and HRTEM is challenging, considering the difference in observed length scale is a few orders of magnitude. However, a preferential flow alignment of the individual layers in anthracene coke was observed and shown in Figure 4-3A. This directionality is the underlying cause of the optical anisotropy observed under the polarized light microscope. Such flow alignment is difficult to observe in HRTEM since structural order in semi-cokes is limited to two dimensions and therefore overlapping projects limit resolution. There is no sign of a flow alignment in the sucrose char. The material is completely isotropic and the layers have a high degree of curvature. The outlined structure in Figure 4-3B shows what appears to be a single wall sphere of 0.7 nm diameter and could be a  $C_{60}$  fullerene or related structure. A second layer partially templates around the fullerene, but does not fully close and stretches off into the material. Values of La, Lc, and the  $d_{002}$  lattice spacing measured with XRD are provided in Table 4-1.

	Anthracene Coke	Sucrose Char
La [nm] from (100)	1.6	1.1
Lc [nm] from (002)	2.6	1.0
d <sub>002</sub> [Å]	3.44	3.77

Table 4-1. XRD crystal structure of anthracene coke and sucrose char.

The results of XRD are in the range of reported values.<sup>3,43,58,60</sup> Anthracene coke has more layers per stack and longer lamellae than sucrose char. However, due to the tortuosity of the lamellae in sucrose char, XRD likely under predicts sucrose char La. The largest observed difference is found in layer plane spacing, anthracene coke has turbostratic spacing where sucrose char has very large layer plane spacing, typical of highly disordered carbon. EELS measurements found both materials to be comprised of ~ 85% sp<sup>2</sup> character, samples were tilted to + and - 40° and the deviation around the mean was found to be 5

percentage points. Of high interest in the investigation into non-graphitizing behavior of sucrose char is the remaining oxygen content. The weight percentages (wt.%) of carbon and oxygen found from EDS in the TEM are 95.7 and 4.3% respectively. The carbon and hydrogen weight percentages found with the CHN analyzer are 92.1 and 4.0%, the remaining 3.9% balance is oxygen since no other elements are present. Thus, the CHN and the EDS are in agreement. When hydrogen is accounted for in the EDS values, carbon and oxygen percentages drop to 92.1 and 4.1 and are in excellent agreement with the CHN values. The starting material, surcose is 51.5 wt.% oxygen and thus carbonization of sucrose at 500 °C removes the majority of the starting oxygen content. It appears already (early on in HTT) that the oxygen is less imporant as compared to the structure it imparts on the carbon material upon evolution. As oxygen is liberated as H<sub>2</sub>O, OH, CO, and CO<sub>2</sub>, the radical left behind controls the resulting cabon nanostrucure and is clearly inducing curvature in the case of sucrose char. This curvature is likely from the formation of odd membered carbon rings, predominantly pentaganol.

## 4.1.2 HTT 1,200 °C - 1 hour

The structural differences built into these materials at the early stage of carbonization (i.e. 500 °C), sets the stage for trajectory of crystallite growth upon additional heat treatment. HRTEM micrographs after HTT of 1,200 °C for a duration of one hour are shown in Figures 4-4 and 4-5 for anthrancene coke and sucrose char, respectively. Anthracene coke begins to resemble a pre-graphitic structure, there is imporved packing and mutual oreintation. The d<sub>002</sub> reamins at 3.44 Å, layer plane spaicing decrease below 3.44 Å does not occur, at least not on reasonble timescales below tempeartures of ~ 2,200 °C.



Figure 4-4. Anthracene coke - HTT 1200 °C for 1 hour.

The complex nanostructure of sucrose char is more pronounced after heat treatment at 1,200 °C. The lamellae stacking is comprised of only a couple layers per stack that are curved at multiple points and are highly intertwined with neighboring material. A few regions possess more ordering with longer La and thicker Lc, see the black arrows in Figure 4-5. The upper arrow is pointing to a ~ 10 nm irregularly shaped enclosed shell particle. The lower arrow is pointing to a structure that resembles the endcap of a multiwall CNT, where the other end connects and grows into the multiwall closed shell particle. Spherical like structures and the half sphere endcaps of CNTs cannot exists without odd membered rings. Oxygen content is below the detectable limit (~ 0.5 atomic %) after HTT of 1,200 °C. The sp<sup>2</sup> content measured with EELS was found to be 93% for anthracene coke and 95% for sucrose char, +/- 5. With such low oxygen and sp<sup>3</sup> character, it seems unlikely that the presence of either can explain the curvature found in this sample.



Figure 4-5. Sucrose char HTT 1200 °C - 1 hour.

# 4.1.3 HTT 2,600 °C - 1 hour

Graphitization heat treatment at 2,600 °C for a hold time of one hour was applied to the virgin coke and char samples. The heat treated samples were prepared for polarized light microscopy to test if optical anisotropy is locked in placed following mesophase development, or if high temperature heat treatment acts to increase the optical texture domain sizes through long range material restructuring. A polarized light micrograph of graphitized anthracene coke is shown in Figure 4-6. Heat treated sucrose char remains completely absent of optical anisotropy, not shown here.



Figure 4-6. Polarized light micrograph of graphitized anthracene coke.

A smooth surface from polishing is difficult to obtain from graphitic samples due to the softness of the material and easy slippage of the layer planes. The black regions in Figure 4-6 are more likely owed to the polishing, rather than isotropic regions. The overall optical texture remains unchanged as compared to virgin anthracene semi-coke. The optical textures are mainly flow domains and domains, sizes were classified in Section 2.1.3 and are described in references 143 and 144.<sup>143,144</sup> A quantitative measure, the optical texture index, was gleaned from both anthracene semi-coke and graphitized anthracene coke from a weighted average of several hundred micrographs collected from the entire polished surfaces. The optical texture indices were found to be statistically equivalent. Therefore, optical anisotropy is locked in placed following mesophase development and thus further illustrates that the key to synthetic graphite production is the mesophase development.

The highly graphitizable anthracene coke produces a synthetic graphite upon graphitization heat treatment as can be seen in the TEM micrograph and SAED pattern in Figure 4-7. In the micrograph the graphite basal planes on the left side are perpendicular to the beam and hence the (002) fringes are transparent, the (100) plane diffracts strongly from this region with preferential alignment as seen by the arc spots in the (100) diffraction ring in the

SAED. Some of the diffracted (100) beam is again diffracted by the underlying (002) planes and shown by the second (002) ring displaced from the direct beam by the (100) beam. The SAED pattern indicates high crystallinity, poly-crystallinity, of this sample as double diffraction, resolution of the (100) from the (101) plane, and the higher order diffracted beams are all attributes of high crystallinity.



Figure 4-7. TEM micrograph (A) and SAED pattern (B) from graphitized anthracene coke.

Sucrose char structure after graphitization heat treatment is shown in Figures 4-8 and 4-9. The structure displayed in Figure 4-8A is representative of the majority of the material observed in the TEM. However, some more ordered structures were found like that displayed in Figure 4-8B. The material is comprised of irregularly shaped pores approximately ~ 10 nm in width. A few particles appear closed, but most are not explicitly closed. The pores may well be inaccessible due to the intertwined structure and would explain the low surface areas and impermeability found from this material.<sup>145</sup> Rouzaud and Oberlin have described this structure as a crumpled up sheet of paper.<sup>145</sup> Resemblance of multiwall CNT endcaps are shown in Figure 4-9, but no CNTs are present. Results of XRD analysis from both materials are given in Table 4-2. The results of XRD further exemplify the extreme differences in theses model graphitizable and non-graphitizable compounds. However, the La from sucrose char is clearly under predicted in XRD as can be seen in the HRTEM images, the intertwined lamellae can be followed for > 30 nm of continuous connectivity in Figure 4-9. The sp<sup>2</sup> content was measured to be ~ 100% for both materials and oxygen content was below the EDS detectable limit. From Equation 2-7 the probability of turbostratic spacing between any random two layers is 7% and 42%, for anthracene and sucrose respectively. The degree of graphitization (g) as defined by Seehra and Pavlovic<sup>146</sup> is 0.93 and 0.58. Where g is:

$$g = (3.44 - d_{002})/(3.44 - 3.354)$$
[4-1]

Table 4-2. XRD crystal structure of anthracene coke and sucrose char- HTT 2600 °C, 1 hr.Anthracene CokeSucrose CharLa [nm] from (110)110.3Lc [nm] from (004)61.7 $g_{002}$  [Å]3.36



Figure 4-8. TEM micrographs of sucrose char - HTT 2600 °C, 1hour.



Figure 4-9. HRTEM micrograph of sucrose char - HTT 2600 °C, 1hour.

# 4.1.4 Co-Carbonization of Anthracene and Sucrose

Depending on precursor, carbonization reactivity can be vastly different. A coke formed through a liquid mesophase requires an extended fluid phase for proper alignment. Anthracene has a relatively fast reactivity as compared to other model coke forming PAH compounds, due to the high free valence indices at the nine and ten position of anthracene, see section 2.1.3. Sucrose also possess a high carbonization reactivity and blends of the two compounds were co-carbonized in a sealed reactor at 500 °C for a duration of 5 hours. In previous co-carbonization studies using anthracene and char forming biphenyl, the anthracene carbonized prior the onset of biphenyl and clear heterogeneity was found in polarized light micrographs, see section 2.1.3. Co-carbonization of a 1:1 blend of anthracene and sucrose results in a homogeneous isotropic char and thus illustrates the overlapping carbonization rates of the two compounds. The co-carbonization of a 3:1 blend of anthracene and sucrose results in a surface comprised mostly of homogeneous texture as shown by the polarized light micrograph in Figure 4-10. Some better developed textures are segregated from the main texture type.



Figure 4-10. Polarized light micrograph of co-carbonized anthracene-sucrose 3:1 blend.

The observed optical texture drops sharply with increased additions of sucrose. Although the anisotropic regions are small, they are present and thus passed through a mesophase during carbonization. The main optical texture is the mosaics texture type (less than 10  $\mu$ m). It is evident from the micrograph that anthracene and sucrose participated together in the formation of the mosaics texture. The anisotropy observed with polarized light microscopy means that there is at least a "sense" of flow direction in the underlying lamellae. What is of most interest is what happens to this structure upon graphitization heat treatment? In the previous section it was demonstrated that anisotropy is locked in placed upon completion of mesophase development. However, the semi-coke produced from the blend of anthracene-sucrose should contain the non-graphitizing elements embedded by sucrose carbonization. The non-graphitizing elements are believed to be mainly pentagonal rings formed after the evolution of oxygen and to a lesser extent cross-linking caused by the remaining oxygen, likely as ether linkages. Oxygen content of the co-carbonized product is 1.2 atomic % as measured with EDS. If odd membered rings are present the annealing trajectory will alter from the standard observed coke graphitization. As the lamellae grow the odd membered rings will induced pronounced curvature and the anisotropy will be lost. A polarized light micrograph of the sucrose-anthracene coke after graphitization heat treatment at 2,600 °C for a duration of one hour is shown in Figure 4-11. The optical anisotropy is completely lost upon heat treatment. This observation shows that if non-graphitizing elements, believed to odd membered rings, can be incorporated into the BSUs formed during mesophase, subsequent heat treatment will act to destroy the optical anisotropy. IUPAC defines coke (passes through mesophase during carbonization) as a graphitizable carbon, while this holds true for most cokes it fails if a coke can be embedded with non-graphitizing elements (i.e. odd membered rings). The texture in Figure 4-11 is absent of segregated domains and suggests that the non-graphitizing elements are also present in the domain textures in Figure 4-10 at a lower concentration.



Figure 4-11. Polarized light micrograph of co-carbonized sucrose-anthracene 3:1 blend - HTT 2,600 °C, 1 hour.

The heat treated material is shown in the TEM micrograph in Figure 4-12. This structure is representative of a mix between that of heat treated sucrose char and anthracene coke. The material is comprised of both branched and fractal like structures and fullerenic-like nanoparticles.



Figure 4-12. TEM micrograph of co-carbonized anthracene-sucrose 3:1 blend - HTT 2,600  $^{\circ}$ C, 1 hour.

Both closed shell ~10 nm diameter particles and CNTs are present. The arrows in Figure 4-13 are pointing to multiwall CNTs. In the TEM micrograph the CNT endcap is directed towards the electron beam and therefore the tube appears to be uncapped. With use angle tilt the CNT was aligned with the end cap visible to the beam, shown in HRTEM micrograph in Figure 4-13.



Figure 4-13. TEM micrographs of multiwall CNTs from co-carbonized anthracene-sucrose 3:1 blend - HTT 2,600 °C, 1 hour.

The fullerene related nanostructures found in this sample supports the notion that odd membered rings are present in char and are the cause of non-graphitizability. However, direct observation of odd membered rings in the virgin char, or shot coke in the case of co-carbonization of sucrose-anthracene is needed to definitively prove the presence of odd membered rings in the starting non-graphitizable material. Dual spherical aberration corrected TEMs like the Titan can provide atomic resolution from accessible single and stable graphene segments. A condition that is not found in amorphous virgin char. Without direct visualization of odd membered rings in the starting non-graphitizable material, the possibility that the odd membered rings present in the heat treated material are manufactured during heat treatment cannot be ruled out.

## 4.2 Oxygen Containing Compounds

If the structure left behind upon oxygen evolution is more important than the oxygen itself, some oxygen containing compounds should result in a structure that is graphitizable. In this section two additional oxygen precursors are investigated: the industrially important non-graphitizable PFA that leads to glassy carbon and closely resembles heat treated sucrose char, and graphitizable anthanthrone. The chemical structures of these compounds are shown in Figure 4-14.



Figure 4-14. Chemical structure of PFA (A) and anthanthrone (B).

Carbonization of PFA produces an isotropic char with no optical anisotropy observed under a polarized light microscope. The nanostructure after carbonization and graphitization heat treatment are shown in the HRTEM micrographs in Figure 4-15. Although the starting char is tortuous and lacking any structural order, the lamellae are longer than virgin sucrose char. This is due to the polymeric material partially maintaining the original shape and thus the non-graphitizability of PFA is not solely due to the oxygen and the potential formation of odd membered rings upon evolution, but also from the high degree of initial crosslinking in the polymer.

The oxygen content in PFA char was measured to be 1.8 wt.% by EDS. The significant oxygen loss (PFA oxygen wt.% ~ 22) during low temperature carbonization is akin to that observed from sucrose. Fitzer and Schafer<sup>147</sup> found oxygen liberation from PFA above 300 °C to be in the form of carbon monoxide and water and simultaneously observed the IR band of C-O-C to decrease. Following the furan rupture the proceeding free radical condensation reactions may or may not result in odd membered ring formation. Their presence would help explain the curvature noted in the heat treated sample in Figure 4-15B. However, the odd membered rings that are present in the half sphere endcaps could have formed out of necessity due to impinging growth of lamellae stacks. When out of plane stacks meet during annealing they tend to form a joint with a noticeable inflection point, see the closed shell polyhedral formation in Figure 2-34. The curvature noted in Figure 4-15B is smooth and not a joint like those found in multifaceted polyhedral particles.



Figure 4-15. TEM micrographs of PFA char (A) and after heat treatment 2,600 °C (B).

To illustrate the importance of carbon intermediate structure after oxygen evolution on graphitizability, model compound anthanthrone was investigated. A polarized light micrograph of carbonized anthanthrone and a TEM micrograph of graphitized anthanthrone semi-coke are provided in Figure 4-16. As seen in Figure 4-16A, anthanthrone goes through mesophase during carbonization as evident by the optical anisotropy. The optical texture is low compared to that of anthracene coke, notice scale bar, but anthanthrone forms a coke nonetheless. Accordingly, the coke transforms to synthetic graphite upon graphitization heat treatment, see the graphite crystal in the TEM micrograph in Figure 4-16B. Crystal parameters found with XRD are given in Table 4-3.



Figure 4-16. Polarized light micrograph of anthanthrone coke (A) and TEM micrograph after HTT of 2,600 °C for 1 hour (B).

Table 4-3. XRD	crystal	structure of	anthanthrone	coke after	·HTT	of 2,600 °	°C for 1	l hour.
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Although less perfect than graphitized anthracene coke, anthanthrone coke is a highly graphitizable carbon and a good graphite precursor. A possible reaction mechanism for the formation of a dimeric molecule of naphthalene (perylene) form anthanthrone is shown in Figure 4-17.



Figure 4-17. Reaction mechanism for formation of perylene from anthanthrone.

Free radical recombination of the intermediate species formed immediately after CO loss would result in five membered rings between the naphthalene molecules. However, due to high bond strain five membered ring do not form adjacent to one another. Consider fullerene, all 12 of the pentagonal rings are isolated from one another by 6 membered rings as adjacent pentagonal rings are unstable. Instead, the naphthalene molecules rotate around the single bond and then free radical recombination forms a dimer (perylene). The remaining two radicals are shown in the end product at the staring locations for book keeping, but are resonant stabilized and can move about the molecule, participate in additional reactions, or be quenched by a hydrogen atom.

This demonstrates that oxygen content is not the cause of non-graphitizability as often considered. The intermediate species formed after oxygen evolution dictates the resulting carbon skeleton and thus the graphitizability. Most often oxygen evolution results in a char and not a coke like in the case of anthanthrone. It is believed that odd membered rings are embedded in the chars formed from oxygen rich precursors upon oxygen evolution. Fullerenic-like structures found in heat treated chars provide circumstantial evidence, but direct observation of odd membered rings in the virgin char has yet to be demonstrated with HRTEM due to the nature of the sample. Since the odd membered rings cannot be directly observed an alternative approach is to knowingly prepare a char with odd membered rings and compare it to chars like sucrose and PFA char, formed from oxygen rich precursors.

## 4.3 The Pentagonal Ring

In this section an attempt is made to directly embed coke and/or char with five membered carbon rings by carbonization of fluorene and co-carbonization of anthracene-fluorene.

### 4.3.1 Carbonization of Fluorene and Subsequent Heat Treatment

Fluorene, a five membered ring containing PAH was selected for carbonization, chemical structure is shown in Figure 4-18. Carbonization at 500 °C for a duration of five hours yielded only tar, no solid carbon. To maintain a prolonged fluid phase that promotes potential mesophase formation, fluorene was again carbonized at 500 °C for five hours and then the temperature was increased to 550 °C and left to soak overnight. A final temperature of 600 °C was held for two hours. The objective of the slow heating was to produce a coke with embedded odd membered rings that upon subsequent heat treatment would result in the destruction of optical anisotropy.



Figure 4-18. Chemical structure of fluorene.

The carbon yield was very high ~ 75%, (e.g. anthracene coke ~ 50%). However, no optical anisotropy was observed under the polarized light microscope up to a magnification of 100X. The polarized light micrograph in Figure 4-19 is absent of colored regions representative of anisotropy.



Figure 4-19. Polarized light micrograph of fluorene char.

The sample was analyzed with a different polarized light microscope using an oil immersion lens, micrographs were taken with a magnification of 625X. Small regions of optical anisotropy were found along some of the pore walls. High gas pressures aid in molecular orientation along pore walls. High gas pressures were present in these pores as gases were heard audibly escaping and accompanied by small "explosive" material discharge as the sample was broken up in preparation for characterization. The high optical rotary power along some regions of the pore walls is demonstrated via stage rotation in the polarized light micrographs in Figure 4-20. The optical anisotropy shown in Figure 4-20 is due to molecular alignment induced by high gas pressures and not mesophase development. Therefore, carbonization of fluorene produces a char and not a coke. The same optical anisotropy located along the pore walls was found after heat treatment at 2,600 °C for 1 hour.



Figure 4-20. Polarized light micrograph of fluorene char with stage rotation.

Fluorene char is useful for the purpose of comparing the nanostructure of a char embedded directly with five membered rings to sucrose and PFA char believed to form five membered rings upon oxygen evolution. This comparison assumes that five membered rings are incorporated into the fluorene char and not entirely thermally rearranged into hexagonal rings prior to inclusion into the char. If similarities are found between fluorene and oxygen precursor chars (sucrose and PFA), it will support the notion that odd membered rings are formed in chars produced from oxygen rich precursors. The structure of fluorene char after heat treatment at 2,600 °C for 1 hour is shown in the TEM micrographs in Figure 4-21.



Figure 4-21. TEM micrographs of fluorene char - HTT 2,600 °C, 1 hour.

This structure bears a striking resemblance to sucrose and PFA heat treated chars, Figures 4-9B and 4-15B. The obvious resemblance in structure between heat treated sucrose and PFA char as compared to heated treated char embedded with five membered rings is evidence that five membered rings are present in the virgin sucrose and PFA char.

Along with the structure in Figure 4-21, multiwall CNT clusters were found, Figure 4-22. The observation of this structure was uncommon, but in each occurrence they were found in clusters with a clear growth direction like that shown in Figure 4-22B. Such organized clusters would be birefringent, with directional dependent index of refraction values and thus may be the cause of the optical anisotropy observed along some of the pore walls. Suggesting that pressure induced their growth, the high pressure gases trapped within the pores of the fullerene char were yet still present after heat treatment. The trapped gases are also a clear indicator of the impermeability of this material, a property shared with glassy carbon formed from PFA.



Figure 4-22. Multiwall CNTs (A) and clusters (B) from heat treated fluorene char.

# 4.3.2 Co-Carbonization of Anthracene-Fluorene and Subsequent Heat Treatment

A 50:50 blend of fluorene and anthracene was co-carbonized at 500 °C for a duration of five hours. The carbonization reactivity of these two compounds are very different. Anthracene having a much faster reactivity at 500 °C. As such the co-carbonization of anthracene-fluorene does not provide a good comparison to the co-carbonization of anthracene-sucrose, as was discussed in Section 4.1.4. Nonetheless, analysis of the co-carbonized anthracene-fluorene product follows. Polarized light micrographs of the co-carbonized product are shown in Figure 4-23.



Figure 4-23. Polarized light micrographs of co-carbonized anthracene-fluorene.

Due to the difference in reactivity of the compounds it was expected that the surface would be heterogeneous and contain optical anisotropic regions formed from anthracene carbonization and pitch from fluorene carbonization. Indeed pitch was found in abundant supply, shown on the edges of the micrographs in Figure 4-23 (black regions) and flow domains from anthracene were abundantly present. Also observed were semi-coalesced mesophase spheres and isolated mesophase spheres, top-center micrograph in Figure 4-23. The mesophase spheres represent a carbonization reactivity that is in-between that of pitch from fluorene and coke from anthracene and thus likely represent co-carbonization regions. Therefore, five membered carbon rings are incorporated into the anthracene-fluorene coke and should act to destroy the optical anisotropy upon graphitization heat treatment. A polarized light micrograph taken from the fluorene-anthracene coke after heat treatment at 2,600 °C for a duration of one hour is shown in Figure 4-24.



Figure 4-24. Polarized light micrograph of fluorene-anthracene coke - HTT 2,600 °C, 1 hour.

After heat treatment the optical texture was partially destroyed as predicted. Two textures were found: mosaics (left) and small domains (right). Likely the mosaics represent regions were more fluorene was included, possibly the mesophase spheres. No flow domains were preserved upon heating and thus fluorene and/or fluorene pitch must have also been embedded in the flow domains present in the virgin coke. The small domains are the remnants of the original flow domains.

At the nanoscale clear heterogeneity exists, as shown in the TEM micrograph in Figure 4-25A. It is for this reason why some of the anisotropy was reserved upon heat treatment and not completely destroyed as was the case for sucrose-anthracene coke.



Figure 4-25. TEM micrographs of fluorene anthracene coke - HTT 2600 °C, 1 hour.

The two regions are synthetic graphite as displayed in the right hand side of Figure 4-25A and disordered regions as shown on the left in Figure 4-25A and with a higher magnification in Figure 4-25B. The disordered regions may have likely been present in the virgin coke as fluorene derived pitch. The disordered region structure is very similar to that observed from heat treated fluorene char. Upon heat treatment, the pitch forms the disordered carbon regions causing stress between adjacent graphitic regions that results in misalignment between the graphitic regions. This misalignment translates to a decreased optical texture size as observed in the polarized light micrographs from before and after heat treatment.

# 4.4 Sulfur

The heteroatom sulfur effects carbon structure in a different way as compared to oxygen. Sulfur is thermally stable in carbon up to ~ 1,000 °C and thus plays little role in the initial low temperature (500 °C) carbonization. As such it imparts a relatively unobservable impact on nanostructure, but rather acts to cause micro-cracks upon rapid evolution in the form of H<sub>2</sub>S and CS<sub>2</sub>, upon subsequent graphitization heat treatment. The micro-cracks result in an observed volume increase and therefore the process has been termed puffing.<sup>41,143,148</sup> This is primarily a problem for the needle coke industry as needle coke is often used as the primary filler in the production of graphite electrodes and micro-cracks act to reduce the electrodes desired properties. In this section a commercial decant oil (DO) with 2.5 wt.% sulfur and a mixture of anthracene and dibenzothiophene are carbonized to produce sulfur containing cokes. The cokes are subsequently graphitized and the effects of puffing are observed.

A mixture of 4:1 anthracene-dibenzothiophene yielded a semi-coke with ~ 3.0 wt.% sulfur, as measured with a Leco sulfur analyzer. The optical texture of the semi-coke is shown in Figure 4-26 and is of the same quality of the pure anthracene derived semi-coke, Figure 4-2A. The DO derived semi-coke is of comparable quality as shown in Figure 4-27 and contains 2.5 wt.% sulfur. Due to the thermal stability of dibenzothiophene, it is expected that the sulfur functionality found in the anthracene-dibenzothiophene semi-coke is thiophenic. In a previous study the sulfur functionality of DO derived semi-coke was found to be exclusively thiophenic, as measured by X-Ray Adsorption Near Edge Spectroscopy.<sup>149</sup>



Figure 4-26. Polarized light micrographs of anthracene-dibenzothiophene coke.



Figure 4-27. Polarized light micrographs of decant oil derived semi-coke.

Upon graphitization heat treatment at 2,600 °C for a duration of one hour, micro-cracks were found in high quantity from both samples. Micro-cracks formed during puffing from anthracene-dibenzothiophene semi-coke are shown in Figure 4-28. Similar quantities of micro-cracks were found in the DO graphitized coke. No sulfur content was detected after graphitization heat treatment. Micro-cracks do occur naturally from the densification process during graphitization heat treatment, but the abundance is far less than that observed from these sulfur containing semi-cokes. A TEM survey showed no observable degradation of the nanostructure due to sulfur evolution. The crystal lattice values measured with XRD are provided in Table 4-4 for both graphitized samples. The two materials are nearly identical. A potential impact due to puffing is seen in the La decrease between graphitized anthracene coke (Table 4-2) and graphitized anthracene-dibenzothiophene is 18%. Brydson and Brown reported a noticeable La decrease due to

puffing from a sulfur containing coke at a HTT of 1,700 °C as compared to 1,500 °C, with recovery of La upon higher HTT.<sup>77</sup> From the findings between anthracene and anthracenedibenzothiophene, it appears that La does not make a full recovery after sulfur evolution.



Figure 4-28. Micro-cracks formed from puffing.

Table 4-4. XRD crystal structure of anthracene-dibenzothiophene and DO coke after graphitization heat treatment.

	Anthracene-	Decant oil
	Dibenzothiophene	
La [nm] from (110)	89.9	94.5
Lc [nm] from (004)	65.4	59.1
d <sub>002</sub> [Å]	3.36	3.36

The La reduction could simply be an effect of the micro-cracks and thus sulfur acts mainly to increase the carbons porosity via micro-crack formation during subsequent graphitization heat treatment.

# 4.5 Summary

The non-graphitizability of chars formed from oxygen rich precursors is believed to be due to the formation of odd membered carbon rings upon oxygen evolution during low temperature carbonization. Upon additional heat treatment the curvature induced from the presence of odd membered rings becomes more pronounced. The fullerenic-like nanostructures found in these heat treated chars supports the notion that odd membered rings are present in the virgin char. However, direct observation of odd membered rings in the virgin char is needed to definitively prove the presence of odd membered rings in the starting non-graphitizable material. Dual spherical aberration corrected TEMs like the Titan can provide atomic resolution, but only from a stable single graphene layer that is properly aligned and accessible. A condition that is not found in virgin char. However, it is not coincidental that the nanostructure of heat treated chars embedded directly with five membered rings bears a striking resemblance to non-graphitizable heat treated chars from oxygen rich precursors.

# **Chapter 5**

# Laser Annealing of Cokes and Chars

In this chapter a Q-switched Nd:YAG laser and a continuous wave  $CO_2$  laser are used to anneal anthracene coke and sucrose char. Anthracene coke and sucrose char were selected for laser annealing because they represent a model graphitizable and non-graphitizable carbon, respectively. Lasers provide rapid heating and cooling with high temporal control. The extent of transformation is kinetically controlled by time above the threshold temperature for transformation. Enabling the annealing trajectories from these two very different carbon materials to be followed with respect to time above temperature. To resolve the nanostructure changes HRTEM is employed.

#### 5.1 Nd:YAG Laser Annealing

As detailed in Section 3.3.1 the Nd:YAG laser pulse width is fixed at ~ 8 ns. The experimental control variable is the laser energy, measured in energy per unit area of the beam (i.e. laser fluence). Samples were heated under an argon atmosphere with fluences of 200, 100, and 50 mJ/cm<sup>2</sup>. These fluences are relatively low as compared to the available fluences in excess of 1,500 mJ/cm<sup>2</sup>. At these fluences samples are directly heated on lacey carbon TEM grids. Direct TEM grid heating is preferred as it provides the best way to evenly disperse the sample and assure uniform heating. Samples were crushed with a mortar and pestle, sonicated in methanol, and drop deposited on TEM grids. Low laser fluences were selected to avoid material sublimation, an undesired process when focus is on thermal annealing. The sublimation temperature of carbon materials is approximately 3,700 °C.<sup>106,113</sup> The C<sub>3</sub> and C<sub>2</sub> sublimation temperatures have been reported to be 3,864 °C and 4,184 °C.<sup>116,128,150</sup> The peak temperatures reached with the fluences used here are ~ 2,800 °C for 50 mJ/cm<sup>2</sup>, 3,500 °C for 100 mJ/cm<sup>2</sup>, and 3,950 °C for 200 mJ/cm<sup>2</sup>. Of the laser fluences used here only 200 mJ/cm<sup>2</sup> results in a maximum temperature above the sublimation point.

Detailed time temperature histories (TTHs) for sucrose char and anthracene coke heated with a 200 mJ/cm<sup>2</sup> laser pulse are shown in Figure 5-1. The error bars represent standard deviation about the mean from three repeated measurements. The time above 3,700 °C is only 30 ns as can be seen from the first 100 ns TTH curve. This is true for both sucrose char and anthracene coke as they have experimentally equivalent TTHs. The TTH is plotted out to 1,700 °C, at which point incandescence signal is weak and the material transformations are frozen in place. The TTHs are divided into the first 100 ns and post 100 ns to illustrate the difference in cooling rate and identify cooling mechanisms. Heating from ambient to ~ 3,300 °C occurs within the first 2 ns of the laser pulse, temperature increases throughout the duration of the laser pulse and the maximum temperature reached is ~ 3,900 °C. The maximum cooling rate of ~ 25 °C/ns from the first five ns following the laser pulse is attributed to sublimation. Once below the sublimation point, conductive cooling is the dominant heat loss mechanism. Radiative cooling is minor in comparison to

conductive cooling at atmospheric pressures and higher. Under vacuum, radiative cooling becomes the dominant mechanisms and typical times above 2,000 °C are around ~ 100  $\mu$ s under vacuum. For the purpose of studying kinetics and trajectories of annealing, shorter times above temperature are desired and thus vacuum heating was not used. The cooling rate decreases as particles cool and the temperature gradient decreases. Following sublimation the cooling rate significantly decreases and becomes progressively slower with decreasing temperature. The total time above 2,200 °C (i.e. IUPAC's defined graphitization heat treatment minimum temperature)<sup>5</sup> is 1.5  $\mu$ s.



Figure 5-1. TTH of sucrose char and anthracene coke - 200 mJ/cm<sup>2</sup> - first 100 ns (A) post 100 ns (B).

The TEM images of laser heated anthracene coke are provided in Figure 5-2. Rather than annealing, the 200 mJ/cm<sup>2</sup> laser pulse ablated the anthracene coke. The energy dense pulse provides energy in excess of all the annealing activation energies. Thus, all activation energies including: devolatilization, conversion of sp<sup>3</sup> hybridized carbon to sp<sup>2</sup> hybridized carbon, lamellae mobilization and growth, reorientation, de-wrinkling, and alignment (d-spacing), occur almost simultaneously. Where thermal annealing has a much slower energy addition rate and therefore traditional furnace annealing steps are delayed based on heating rate and occur in a step wise fashion. By providing the energy needed for lamellae to become highly mobile prior to La growth and reorientation acting to anchor them down, they are able to break free of the material. Upon rapid cooling the ablated layers form the chaotic fullerenic-like nanostructure out of necessity to terminate reactive edge sites, structure shown in Figure 5-2B.



Figure 5-2. TEM images of anthracene coke - 200 mJ/cm<sup>2</sup>.

Therefore, rapid heating via laser annealing results in an altered annealing trajectory. Due to the unknown extent of vaporization and impact on structure, laser heating with 200 mJ/cm<sup>2</sup> cannot be directly compared to traditional annealing.

TEM images of sucrose char after laser heating with a 200 mJ/cm<sup>2</sup> laser pulse are provided in Figure 5-3. Most of the starting 4.1 wt.% oxygen in sucrose char is liberated. The oxygen content in the EDS elemental map in Figure 5-3A is 0.9 wt.%. The retained oxygen may be due to kinetic constraints imposed by rapid cooling, some of the liberated oxygen may be reincorporated into the carbon matrix upon cooling. The EDS map also highlights the carbon thickness contrast and the heterogeneity in the structure is characteristic of ablation, Figure 5-3A. The nanostructure of sucrose char is similar to that found after annealing at 1,200 °C for a duration of one hour, Figure 4-5 vs Figure 5-3B. The major structure type found is lamellae with only a couple layers per stack that are curved at multiple points and are highly intertwined with neighboring material. A few regions possess more ordering with longer La and thicker Lc, like that shown in Figure 5-3C. For sucrose char, similarities appear between laser and traditional annealing. Lower laser fluences (i.e. lower maximum temperatures) are used to avoid vaporization and provide a more direct comparison to traditional furnace annealing. The TTHs for sucrose char and anthracene coke heated with a 100 mJ/cm<sup>2</sup> laser pulse in an inert gas environment are shown in Figure 5-4.



Figure 5-3. EDS map (A), HRTEM micrographs (B and C) of sucrose char - 200 mJ/cm<sup>2</sup>.



Figure 5-4. TTHs of sucrose char and anthracene coke -  $100 \text{ mJ/cm}^2$  - first 100 ns (A) post 100 ns (B).

Although the maximum temperature is well below the sublimation point, the first five ns of cooling after peak temperature occur at a rate (15  $^{\circ}C/ns$ ), faster than the possible

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combination of conductive and radiative cooling mechanisms alone. This rapid initial cooling, not caused via vaporization, must be due to material ablation. Following the initial cooling, the TTH profiles follow the same trend as previously discussed. Anthracene coke and sucrose char have similar material properties upon laser heating, shown in the HRTEM micrographs in Figure 5-5.



Figure 5-5. TEM micrographs after laser heating with  $100 \text{ mJ/cm}^2$  - anthracene coke (A-B) and sucrose char (C-D).

The maximum temperature reached (~ 3,500 °C) is a couple hundred °C below the sublimation point. Yet, significant material ablation occurred. This demonstrates that upon rapid heating all annealing activation energy are reached simultaneously and causes the trajectory to deviate from traditional furnace annealing. The overall extent of ablation is less between the 100 and 200 mJ/cm<sup>2</sup> laser heated samples. The interiors of the particles from both anthracene and sucrose are unaltered after laser heating with 100 mJ/cm<sup>2</sup> laser pulse. This is due to the limited skin depth of 1064 nm laser light, calculated in Section 3.3.1. With decreasing laser energy the depth of heating decreases as laser beam intensity is lost with depth.

The TTHs for sucrose char and anthracene coke heated with a 50 mJ/cm<sup>2</sup> laser pulse are shown in Figure 5-6.



Figure 5-6. TTHs of sucrose char and anthracene coke - 50 mJ/cm<sup>2</sup>.

The low fluence results in low incandescence signal and wider camera gate widths are required to collect adequate signal for temperature determination. The TTHs in Figure 5-6 are integrated average temperatures, with collection widths as wide as 500 ns. The peak temperature of ~ 2,800 °C is the integrated average temperature of the first 50 ns of incandescence signal. The true peak temperature occurring just after the laser pulse is likely higher, but not by much. For example, the peak temperature found with a 5 ns gate width from 200 mJ/cm<sup>2</sup> is 3,940 °C and the average integrated temperature from the first 50 ns is 3,850 °C. Where the average of the ten temperature measurements taken in 5 ns intervals over the first 50 ns is 3,760 °C. The first 50 ns time integrated temperature is higher than the average of the ten temperature measurements taken in 5 ns intervals over the first 50 ns. This is because higher temperatures have higher radiative intensity and thus integrated average temperatures are biased to the higher initial temperatures. Due to the low incandescence signal, the initial cooling rate immediately after peak temperature is unknown and cannot be used to make inference about the possibility of ablation based on the TTH alone. The total incandescence signal is related to both maximum temperature and quantity of heated sample. Therefore, it is obvious that little sample was heated from the 50 mJ/cm<sup>2</sup> laser pulse due to the low signal intensity. Limited transformed sample was found upon TEM investigation, small regions of annealed/ablated material were found and shown in the TEM micrographs in Figure 5-7. The anthracene coke structure in Figure 5-7A is more graphitic as compared to heating with high laser fluences, graphitic bands are seen in the ablated material. The laser heated material is not fully ablated (discharged) from the material as it is still connected to the original particles. It appears that the heated surface layers are peeled off and expand out away from the relatively cool underlying particle. The partially ablated regions are small and would be heated uniformly by additional pulses. Anthracene coke was used for multiple pulse heating as a variation in annealing trajectory

relative to traditional heating is more easily seen from this sample. An HRTEM image after heating with ten pulses of 50 mJ/cm<sup>2</sup> is provided in Figure 5-8.



Figure 5-7. TEM micrographs of anthracene coke (A) and sucrose char (B) - 50 mJ/cm<sup>2</sup>.



Figure 5-8. TEM micrographs of anthracene coke - 10 pulse - 50 mJ/cm<sup>2</sup>.

The structure after ten pulses is highly fullerenic-like and comprised mainly of ~ 5-10 nm closed shell quasi-spherical particles. This shows that even at low laser fluences, energy dense Q-switched laser pulses cannot be used to study annealing at these short timescales. Material ablation is the dominant effect at these rapid heating rates ~330,000,000,000 °C/s

at 50mJ/cm<sup>2</sup>. Rapid heating causes the initial deviation from traditional furnace annealing pathway by simultaneously activating all activation energies. Kinetics also play a role in annealing pathway as the time at elevated temperature is limited (time above 2,000 °C is 1.5  $\mu$ s). At these short times above the threshold temperature, the long range material motions are kinetically limited. Regardless of additional pulses, the total consecutive time at temperature is never long enough for long range material restructuring to occur.

## 5.2 CO<sub>2</sub> Laser Annealing

Laser pulse widths of 100 microseconds to five minutes were used during CO<sub>2</sub> laser annealing experiments. The earliest detected temperature collected from the first few microseconds of LII signal is approximately 1,600 °C and temperature increases to a maximum of ~ 2,600 °C gradually over a duration of 1.3 ms. The CO<sub>2</sub> laser heating rate is slow in comparison to the Nd:YAG laser heating rates and the annealing trajectory is predicted to follow the traditional annealing pathway. The maximum temperature is constant for the duration of the laser pulse. Cooling is dependent upon quantity of heated sample and pulse duration, cooling times are on the order of tens of ms. Slower heating rates and a lower maximum temperature results from the use of the beam expander. No LII signal is detected during the first few ms of annealing with use of the beam expander. After a 5 ms delay the samples are ~ 1,000 °C and a temperature of ~ 1,200 °C is reached within an additional ms. A maximum temperature of ~1,700 °C is reached slowly over the duration of a second. Pulse width modulation was used in concert with the beam expander for the purpose of limiting maximum temperature to 1,200 °C. Rapid cycling the radio frequency signal (faster than the rise and fall times of laser medium) acts to reduce power and maintain a true continuous wave laser beam. Anthracene coke and sucrose char were laser heated to 1,200 °C and 2,600 °C and held for varying durations. The transformations are compared to traditional furnace heating at 1,200 °C (Figures 4-4 and 4-5) and 2,600 °C (Figures 4-7 and 4-8) for a one hour duration.

# 5.2.1 CO<sub>2</sub> Laser Annealing - 1,200 °C

Samples were directly heated on copper supported lacey carbon TEM grids. The grids survive, for the most part, the short times at 1,200 °C. Direct TEM grid heating is preferred as it provides the best way to evenly disperse the sample and assure uniform heating. Samples were crushed with a mortar and pestle, sonicated in methanol, and drop deposited on the TEM grids. The TTHs for sucrose char and anthracene coke heated with a 20 s laser pulse in an argon atmosphere are shown in Figure 5-9. Full power was used to heat the samples to the desired temperature of 1,200 °C. Power was reduced to 85% for the remainder of the pulse duration. This power provides a stable isothermal temperature of 1,200 °C throughout the remainder of the laser pulse. Samples cool to temperatures below the detection limit of ~ 1,000 °C in ~ 50 ms after laser pulse extinction. HRTEM micrographs after annealing for 2.5 seconds are displayed Figure 5-10.



Figure 5-9. Heating rates (A), temperature stability during laser pulse (B), and cooling rates (C) for anthracene coke and sucrose char heated with expanded beam  $CO_2$  laser radiation.



Figure 5-10. HRTEM micrographs of anthracene coke (A) and sucrose char (B) after heat treatment at 1,200 °C for 2.5 seconds.

The laser annealed anthracene coke is structurally equivalent to that found from furnace heating at 1,200 °C (Figure 4-4). The sucrose char is similar, but yet incomplete as compared to furnace (Figure 4-5). After 5 s at 1,200 °C sucrose char transformations are complete and the structure is nearly equivalent to furnace annealing, as shown in the HRTEM micrograph in Figure 5-11.

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Figure 5-11. Sucrose char after heat treatment at 1,200 °C for 5 seconds.

The transformation of sucrose char requires more time above temperature than anthracene coke to reach completion. Sucrose char lamellae have an arduous path towards restructuring due to the curvature and intertwined nature of the lamellae as compared to anthracene coke, which is comprised of rudimentary parallel stacks due to mesophase development. Therefore, the slower annealing rate of sucrose char is not surprising. At 1,200 °C visible changes were subtle from samples heated for one second. The structure found after annealing with a one second pulse is shown in Figure 5-11. The anthracene coke d<sub>002</sub> spacing actually increases to 3.47 Å from 3.44 Å after laser annealing at 1,200 °C for one second. This retrograde step is found in traditional HTT based experiments (i.e. long duration isothermal heating) where cokes reach a first Lc maximum and spacing minimum, followed by degradation with increasing HTT and then re-established order upon much higher HTT.<sup>43,64</sup> However, the retrograde step has been reported to occur around 650 °C. Here it occurs at 1,200 °C and thus this is a kinetic first step in annealing. The retrograde step can be explained by considering the initial nearly parallel alignment of the PAHs after mesophase development that then bond to neighbors which may not be in the same preferred orientation. Although the layer spacing is slightly increased, the material crystallinity increases as can be seen by the 002 arc spots in the SAED pattern insert in Figure 5-12A. This directionality is not as apparent in virgin anthracene coke. Both samples appear to have experienced a slight increase in lamellae length. The dark spots in the sucrose char micrograph are copper from melt expulsion of the Cu grid.



Figure 5-12. HRTEM micrograph and SAED pattern of anthracene coke (A) and HRTEM micrograph of sucrose char (B) after heat treatment at 1,200 °C for 1 seconds.

As shown both samples anneal to furnace equivalent structures. Therefore,  $CO_2$  laser annealing is equivalent to furnace annealing at these times above temperature with a heating rate of 200,000 °C/s and a maximum temperature of 1,200 °C.

#### 5.2.2 CO<sub>2</sub> Laser Annealing - 2,600 °C

To reach graphitization heat treatment temperature the beam expander was removed and the laser was operated at full power. The TTHs for sucrose char and anthracene coke heated with a 20 s laser pulse are shown in Figure 5-13.



Figure 5-13. Heating rates (A), temperature stability during laser pulse (B), and cooling rates (C) for anthracene coke and sucrose char heated with  $CO_2$  laser radiation.

A maximum temperature of ~ 2,600 °C is reached in 1.4 ms at a rate of ~1,840,000 °C/s. The maximum temperature is isothermal throughout the laser pulse. Temperatures fall below 2,000 °C within 100 ms, at which point material transformations are frozen in place.

At this temperature, the TEM grids do not survive pulses longer than half a second and material transformations are far from complete at this time. Since direct grid heating was not possible samples were ground down to fine powder and a very thin layer was directly heated in a small recessed hole in a graphite crucible. Thin samples were used to promote uniform heating. This approach was determined appropriate based on TTHs collected from underneath a thin layer. A carbon planchet with a hole drilled out for optical access was used to measure temperature from the underlying surface of the thin layer (couple hundred  $\mu$ m). The thin layer was prepared by pressing powdered sample. An aperture was used to collect LII signal from just the bottom of the laser heated sample, avoiding contributions from the conductively heated planchet. A comparison of heating and maximum temperature from the top surface and bottom surfaces of sucrose char are displayed in Figure 5-14. Anthracene coke followed the same trend.



Figure 5-14. Heating rates and maximum temperature from the top and bottom surfaces of sucrose char.

Detectable LII signal is delayed 400  $\mu$ s from the bottom relative to the top surface and an additional ~ 2 ms are required before the sample reaches thermal equilibrium. The bottom surface temperature remains ~50 °C less than the top surface.
### 5.2.2.1 CO<sub>2</sub> Laser Annealing of Anthracene Coke - 2,600 °C

Annealing steps of graphitizable carbons follow the well-known thermodynamically based HTT diagram shown in Figure 2-25. Where stage 1 at 500 °C represents the BSUs formed from mesophase. Stage 2 occurs at 1,000 °C when the BSUs associate face to face into distorted columns. Stage 3 occurs around 1,500 °C when the columns coalesce into wrinkled layers. Stage 4 begins above 1,700 °C when the distorted layers stiffen and become perfectly flat. Following the four stages outlined by Oberlin<sup>47</sup>, the layer plane spacing slowly decreases as layers assume graphitic lattice spacing at temperatures above 2,200 °C.

The CO<sub>2</sub> laser rapidly heats carbon samples to graphitization heat treatment temperature. The ramp rate of ~1,840,000 °C/s brings the sample to 2,600 °C in 1.4 ms. Noticeable restructuring occurs after annealing for a duration of 250 ms, as displayed in the HRTEM micrograph in Figure 5-16 and compared to the HRTEM micrograph from virgin coke in Figure 5-15. The crystalline directionality is more pronounced. An increase in crystalline order is clearly displayed in the SAED pattern. Virgin coke possess only diffuse diffraction rings from the (002) and (100) planes. After annealing for 250 ms arc spots are seen in the SAED pattern showing both the (002) and higher order (004) planes. This transition represents stage 2 (i.e. the BSUs in the virgin coke associate face to face into distorted columns). The extent of transformation after 250 ms at 2,600 °C is equivalent to that of annealing at 1,200 °C for a duration of 2.5 seconds and thus demonstrates the high rate dependence on temperature. The distorted columns coalesce into wrinkled layers in stage 3 and occur within one second at 2,600 °C, as displayed in Figure 5-17A. After annealing for five seconds the layers becomes stiff and straight, as seen in Figure 5-17B, and represents the completion of the well-known annealing steps shown in Figure 2-25. With additional time above temperature the ordering is best observed by the increase in crystallinity (i.e. three dimensional graphitic order), measured by the decrease in  $d_{002}$ spacing, provided in Table 5-1. Additionally, the degree of graphitization (g) is given in Table 5-1, see Equation 4-1.

2,000 0.		
Time [s]	d <sub>002</sub> [Å]	g
0	3.44	0
0.25	3.44	0
1	3.44	0
5	3.42	0.23
60	3.40	0.46
300	3.39	0.58

Table 5-1.	Layer pla	ane sp	pacing	and	degree	of	graphitization	with	respect	to	time	above
2,600 °C.												

From these results it is seen that the two dimensional annealing steps and layer plane dewrinkling are completed within the first five seconds above 2,600 °C. Graphitization as quantified by a reduction in layer plane spacing below 3.44 Å does not occur until the completion of the two dimension ordering. Upon initiation of graphitization, the spacing reduction initially occurs at a faster rate and progressively slows. During the first one minute of graphitization the layer plane spacing decreases at a rate of 0.04 Å/min. After the first minute the rate of graphitization decays and a spacing reduction of only an additional 0.01 Å is achieved after an additional four minutes at 2,600 °C (i.e. 0.0025 Å/min). The layer spacing from anthracene coke graphitized in a furnace at 2,600 °C for a duration of one hour is 3.36. Thus, the spacing reduction between five minutes and one hour may proceeded at a rate of 0.00055 Å/min. The trajectory and steps of annealing follow the traditional pathway and therefore CO<sub>2</sub> laser annealing is equivalent to traditional annealing.



Figure 5-15. HRTEM micrograph (A) and SAED pattern (B) of virgin anthracene coke.



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Figure 5-17. HRTEM micrographs of anthracene coke after CO<sub>2</sub> laser annealing for one second (A) and five seconds (B).



Figure 5-18. HRTEM micrographs of anthracene coke after  $CO_2$  laser annealing for one minute (A) and five minutes (B).

### 5.2.2.2 CO<sub>2</sub> Laser Annealing of Sucrose Char - 2,600 °C

As seen in the previous section,  $CO_2$  laser annealing of graphitizable anthracene coke is equivalent to traditional furnace annealing. In this section non-graphitizable sucrose char annealing trajectories with respect to time are observed. Sucrose char lamellae have an arduous path towards restructuring due to the curvature and intertwined nature of the lamellae in sucrose char as compared to anthracene coke. The pathway towards final annealed product is highlighted in the TEM micrographs shown in Figures 5-19 to 5-26. The end structure obtained after annealing for 30 seconds is equivalent to the structure found from traditional furnace heating at 2,600 °C for a duration of one hour, Figures 4-8 and 5-25. Therefore,  $CO_2$  laser annealing with a heating rate of 1,840,000 °C/s is equivalent to traditional annealing for both graphitizable and non-graphitizable carbons. Considering the final annealed products are equivalent, the trajectories observed here during short pulse durations are also likely occurring in traditional furnace heating, yet undetectable due to limited temporal control.

The earliest observable material transformations occur after 250 ms of annealing as displayed in Figure 5-21B. Compared to the virgin char in Figure 5-29A, the annealed sample lamellae appear slightly longer and have more pronounced curvature. The oxygen content is below the EDS detection limit. The structure after 250 ms still has a long way to go before reaching the final equilibrium structure. Therefore, oxygen evolves out early in the annealing process and acts to impact annealing trajectory via the structure it leaves behind upon evolution and not by direct C-O-C cross-linking. The structure after one second is shown in Figure 5-20. The arrow in the micrograph is highlighting what appears to be the early formation of a two layer quasi-spherical closed shell nanoparticle. The odd

membered rings hypothesized to exist in sucrose char should lead to the formation of structures with high curvature as the neighboring lamellae bond together. The structure after annealing for five seconds is shown in Figures 5-21 and 5-23. The curvature after five seconds at 2,600 °C exceeds all expectations and clearly demonstrates that an abundance of odd membered rings are present. The spherical closed shell nanoparticles could not exist without inclusion of odd membered rings.

The nanostructure of sucrose char after five seconds of isothermal annealing at 2,600 °C is comprised almost entirely of quasi-spherical closed shell particles. A tilt series of HRTEM micrographs are provided in Figure 5-22 for the purpose of verifying the three dimensional shape (i.e. quasi-spherical). The presence of hollow shell structures is observed without stage rotation (B), with stage rotation of  $45^{\circ}$  (C) the hollow shells are observed and can be compared against projections without stage rotation. The arrows in B and C highlight a hollow pentagonal shaped three layer particle. The hollow structure is not observed from projection at -45° (A), but rather the particles appear onion like. The onion like appearance at -45° is due to multiple projections. The material thickness the electron beam must travel is greater at  $-45^{\circ}$ , as seen by the reduction in width as compared to  $0^{\circ}$  (i.e. long dimension aligned parallel to electron beam at -45°). Since nanostructure dictates annealing trajectory propagation direction, it would be expected that closed shell structures would remain closed upon additional heat treatment and perhaps take on the polyhedral closed shell structure as a final product. Although some closed structures are observed in the final traditionally annealed sucrose char, the structure is mainly comprised of irregular cage-like pores that are not explicitly closed. If CO<sub>2</sub> laser annealing is equivalent to furnace annealing the closed shell structures must open upon additional heat treatment. Indeed closed shell structures are obliterated with additional heat treatment and give rise to the formation or irregularly shaped pores formed from shell opening. Opened particles are displayed in the micrographs in Figure 5-24, taken after annealing for a duration of ten seconds. Shell opening can be explained by considering the sharing of walls between particles and the extension of some of the wall layers extending out away from the particles as highlighted in Figure 5-23. The bottom wall of the pentagonal shaped hollow particle (2-dimensional projection of a "house-like" structure) in Figure 5-23 is comprised of five layers. However, at the corner two of the layers branch off into the material and do not continuous wrap the particle. With additional annealing the layers that branch off will act to pull on the pentagonal particle and cause it to unravel. As the pentagonal structure opens it applies a stress on the already highly strained box like particle it shares one of the top walls with and causes it to open as well. This type of unraveling and propagative particle opening occurs throughout the material. The material continues to anneal with additional heat treatment and reaches an end structure that is equivalent to traditional furnace annealing in 30 seconds as seen by comparing Figure 5-25 with Figure 4-8.

The CNT endcap like structures found in furnace annealed sucrose char are really the remnants of once closed fullerenic-like nanoparticles. Odd membered rings are required for the existence of such structures. Therefore, the odd membered carbon ring induced curvature found in furnace annealed sucrose char is not manufactured during annealing via impinging growth, but rather the odd membered rings are present in the virgin char.



Figure 5-19. HRTEM micrographs of virgin sucrose char (A) and after 0.25 seconds of CO<sub>2</sub> laser annealing (B).



Figure 5-20. HRTEM micrograph of sucrose char after one second of CO<sub>2</sub> laser annealing.





Figure 5-22. HRTEM micrographs of sucrose char after five seconds of  $CO_2$  laser annealing. Stage tilt: -45° (A), 0° (B), and 45° (C).



Figure 5-23. HRTEM micrograph of sucrose char after five seconds of CO<sub>2</sub> laser annealing.





Figure 5-25. TEM micrographs of sucrose char after 30 seconds of CO<sub>2</sub> laser annealing.



Figure 5-26. HRTEM micrograph of sucrose char after 30 seconds of CO<sub>2</sub> laser annealing.

### 5.3 Summary

The energy dense Nd:YAG Q-switched laser heats carbon above graphitization heat treatment temperature within nanoseconds and material ablation is the dominant effect. The material transformation trajectory is altered verses traditional furnace heating at these rapid heating rates ~330,000,000,000 °C/s and short time at elevated temperature. A continuous wave CO<sub>2</sub> laser heats carbon samples to graphitization heat treatment temperature with a ramp rate of ~1,840,000 °C/s and brings the sample to 2,600 °C in 1.4 ms. At this heating rate and time scale, samples followed the traditional furnace annealing pathways as based upon the equivalent end structures obtained from matching temperatures. Pulsing the CO<sub>2</sub> laser with a pulse generator allowed for the trajectories with respect to time above temperature to be followed. Graphitizable anthracene coke anneals faster than non-graphitizable sucrose char. Sucrose char passes through a structural state of completely closed shell nanoparticles that open upon additional heat treatment and give rise to the irregular pore structure found in the end product. The observed curvature in sucrose char annealed at 2,600 °C is a result of shell opening and thus odd membered rings are not manufactured during the annealing process due to impinging growth of stacks, but are present in the starting structure.

# **Chapter 6**

### Laser Annealing of Carbon Black

Carbon black imposes natural geometric constraints in that primary particles are spherical nanoparticles and aggregate morphology is a collection of primary particles. Primary particles typically have a diameter in the range of 20-100 nm and are volumetric absorbers of both 1064 nm and 10.6  $\mu$ m laser light (i.e. uniform heating). The semi-isolated nature of the primary particles enables easy observation of nanostructure material transformation as such change is largely constricted to within the primary particles. Annealing extent of carbon black is controlled by a progressive set of length scales: a) initial morphology controls the extent of nanostructure propagation, b) nascent nanostructure controls the direction of nanostructure evolution. In this chapter the structural and chemical transformations upon laser annealing a commercial carbon black and laboratory generated synthetic soots are investigated with HRTEM and image analysis. The laser heated samples are compared to traditional furnace heating at a temperature of 2,600 °C for a one hour duration.

#### 6.1 Nd:YAG Laser Annealing

Nd:YAG laser heating of anthracene coke and sucrose char resulted primarily in ablation as was demonstrated in Section 5.1. Carbon black is more resistant to ablation. Carbon blacks are formed under higher temperatures than cokes and chars and thus have higher carbon to hydrogen ratios, making them more resilient to ablation. To test the dependence of initial structure and hydrogen content with respect to ablation, anthracene coke annealed at 1,200 °C for a duration of one hour (see Figure 4-4) was heated with the Nd:YAG laser, results provided in the Appendix. The commercial carbon black used in this section has a hydrogen wt.% of 0.25 as compared to virgin anthracene coke and sucrose char at 4 wt.%. Additionally, the small particles are in the Rayleigh range and are volumetric absorbers. Therefore, the added ablation resistance found in carbon black may be credited to uniform particle heating where the heated surface layers are peeled off from the relatively cool underlying coke and char particles. Regardless of the reason for the added ablation resistance as compared to coke and char, carbon black provides a test specimen to study annealing with increasing Nd:YAG laser fluence and pulse number. A two by two matrix with increasing fluence (i.e. temperature) and pulse number (i.e. time) is used here to anneal a commercial carbon black (Cabot R250). The nascent structure of R250 was provided in Figure 2-3. The structure after graphitization heat treatment in a furnace at 2,600 °C for a one hour is provided in Figure 6-1. After heat treatment the primary particles are multifaceted polyhedral structures with hollow centers.



Figure 6-1. TEM micrographs of R250 after heat treatment for one hour at 2600 °C.

The carbon black templates out towards the perimeter leaving behind the hollow center. The centers of nascent carbon black are comprised of disorganized PAHs that acted as the particle nuclei.. The outer layers are longer and more rigid, see HRTEM micrograph in Figure 2-3B. The carbon hybridization is also different between the center of the particle and the exterior. EELS spectra were collected from both the center and exterior in STEM mode and the measured sp<sup>2</sup> was 88 and 93% from the center and edge respectively.

### 6.1.1 Fluence

The structural transformations are observed from heating R250 with a wide range of laser fluences. The fluences include: 25, 50, 100, 200, 300, and 550 mJ/cm<sup>2</sup>. The TTHs collected from heating a powder bed of carbon black under an argon atmosphere are experimentally equivalent to those collected from anthracene coke and sucrose char. The maximum observed temperature increases approximately linearly between 25 to 100 mJ/cm<sup>2</sup>. At fluences  $\geq$  300 mJ/cm<sup>2</sup> the maximum observed temperature is constant at ~ 4,177 °C ± 40 °C and is in agreement with the reported C<sub>2</sub> sublimation temperature of 4,184 °C.<sup>106,117,122,128</sup> Peak temperatures with respect to fluence are plotted in Figure 6-2. The maximum temperature moves to earlier times with an increase in fluence above 300 mJ/cm<sup>2</sup>. The maximum temperature occurs during the latter half of the 8 ns laser pulse at fluences below 300 mJ/cm<sup>2</sup>. At 550 mJ/cm<sup>2</sup> the earliest detected temperature (first five ns of the laser pulse) is the sublimation temperature of ~ 4,184 °C. The first 100 ns TTHs for R250 heated with 550 and 200 mJ/cm<sup>2</sup> are shown in Figure 6-3. The maximum temperature remains constant throughout the pulse, followed by rapid cooling via vaporization. The maximum cooling rate is ~ 25 °C/ns during the first 20 ns following the laser pulse and is

attributed to vaporization. Once below the sublimation point conductive cooling is the dominant heat loss mechanism. Radiative cooling is minor in comparison to conductive cooling at atmospheric pressures. Extended cooling profiles follow those already provided in Section 5.1.



Figure 6-2. Peak temperature with respect to fluence.



Figure 6-3. First 100 ns TTHs profiles from 200 and 550 mJ/cm<sup>2</sup>.

Annealing with 25 mJ/cm<sup>2</sup> gives a peak temperature of ~ 2,400 °C  $\pm$  30 °C. At this low fluence material transformation is limited, the extent of transformation is displayed by the

HRTEM micrograph in Figure 6-4A. Some small gaps can been seen in between the material. However, visually the lamellae appear the same as compared to nascent R250. When observed under the electron beam the laser induced voids quickly (within seconds) collapse. The collapsing is illustrated progressively between images A, B and C. The structure in C is visually equivalent to nascent carbon black.



Figure 6-4. HRTEM micrographs of R250 - 25 mJ/cm<sup>2</sup>.

The electron beam was spread to reduce intensity and knock-on damage. The beam was not parked on the sample for any extended duration, carbon blacks are typically stable under the beam. Therefore, the accordion motion means that the laser induced changes are not locked in place (i.e. neighboring lamellae are not bonded and locked in position). With increasing fluence the laser induced changes are locked in. A HRTEM micrograph of R250 heated with a 50 mJ/cm<sup>2</sup> laser pulse is shown in Figure 6-5.



Figure 6-5. HRTEM micrograph of R250 - 50 mJ/cm<sup>2</sup>.

The laser induced changes after heating with 50 mJ/cm<sup>2</sup> and reaching a maximum temperature of ~ 2,850 °C  $\pm$  40 °C are stable under the electron beam. The increased stability is due to long range connectivity of the lamellae that wrap the circumference of each concentric shell. Larger void spaces are observed as compared to heating with 25 mJ/cm<sup>2</sup>.

Vaporization is observed after heating with 100 mJ/cm<sup>2</sup> and a maximum temperature of  $3,500 \pm 40$  °C. Although ~ 200 °C below the commonly reported sublimation temperature for carbon, solidified carbon vapor is found and highlighted by arrows in Figure 6-6A. The amorphous carbon formed from solidified vapor is likely not from C<sub>3</sub> or C<sub>2</sub> sublimation due to temperature and no C<sub>2</sub> swan band emission was observed in the spectra. The disorganized PAH centers along with some of the exterior layers are ablated/vaporized at this high heating rate of 437,750,000,000 °C/s. The micrograph in Figure 6-6B shows a branch of the original aggregate that was blasted off and reattached by solidified vapor. This represents significant vaporization/ablation at this yet, relatively low fluence. The nanostructure is shown in the HRTEM micrographs in Figure 6-7.



Figure 6-6. TEM micrographs of R250 - 100 mJ/cm<sup>2</sup>.



Figure 6-7. HRTEM micrographs of R250 - 100 mJ/cm<sup>2</sup>.

The arrow in Figure 6-7A shows a region that is highly disordered. This disorder represents an exit point for vaporized material and thus explains the disorder as compared to the connected neighboring lamellae. Ablation/vaporization of the interior of a particle is displayed in Figure 6-7B. As compared to 50 mJ/cm<sup>2</sup>, annealing with 100 mJ/cm<sup>2</sup> results in disorder and is attributed to ablation and vaporization. At 200 mJ/cm<sup>2</sup> and a maximum

temperature of ~ 3,900 ± 40 °C the observed structures are similar to those from 100 mJ/cm<sup>2</sup> heating, with increased ablation and vaporization. The formation of new particles formed from vaporization were observed both attached and isolated. A new particle formed from vaporization is displayed in Figure 6-8B. The maximum temperature is above the C<sub>3</sub> sublimation temperature of 3,864 °C<sup>122,128</sup> and extent of vaporization at 200 mJ/cm<sup>2</sup> is increased as evident by the isolated particles. Vapor velocity increases with temperature and a decrease in vapor species size, such vapor escapes the aggregate completely and creates isolated particles.



Figure 6-8. HRTEM micrographs of R250 - 200 mJ/cm<sup>2</sup>.

At 300 mJ/cm<sup>2</sup> the maximum temperature is 4,177 °C  $\pm$  40 °C and is in agreement with the reported C<sub>2</sub> sublimation temperature of 4,184 °C.<sup>106,117,122,128</sup> At this fluence C<sub>2</sub> plasma emission is observed in the spectra. To avoid interference in black body temperature extraction, plasma regions are masked out of the black body temperature fit. With increased vaporization the particles either partially rupture or explode completely as shown in Figures 6-9 A and B, respectively. The hole in A tears completely through the particle and B shows a completely ruptured particle. At 550 mJ/cm<sup>2</sup> the remnants of carbon black are elongated and straightened ribbons as shown in Figure 6-10. At 550 mJ/cm<sup>2</sup> vaporization is significant as can be inferred from the strong plasma signal as displayed in Figure 6-11A. The Na 2P line at 589, the K (II) line at 612, and the K (I) doublet at 766 and 769 nm shown in the spectra were likely introduced into the carbon black during the manufacturing process. The potassium doublet is resolved using a higher resolution diffraction grating (1200 groves/mm) and shown in Figure 6-11B. Disordered regions and regions with high strain due to bond angle are preferentially removed via vaporization. The material left behind is the elongated and straightened ribbon structure.



Figure 6-9. HRTEM micrographs of R250 - 300 mJ/cm<sup>2</sup>.



Figure 6-10. HRTEM micrographs of R250 - 550 mJ/cm<sup>2</sup>.



Figure 6-11. Plasma signal from R250 - 550 mJ/cm<sup>2</sup>.

#### 6.1.2 Pulse Number

For the pulse number experiment a fluence of 50 mJ/cm<sup>2</sup> was selected because as shown in the previous section, this fluence does not result in vaporization or apparent ablation. Additionally, the structure after one pulse as shown in Figure 6-4 appears as if it is on course to anneal in a similar fashion to the furnace heated structure, shown in Figure 6-1. Additional time above temperature is provided by additional laser pulses. The material was heated with 1, 2, 3, 4, 10, and 100 pulses. The changes from 1-4 pulses are quantified by HRTEM image processing codes as described in Section 3.4.4. The quantification includes measurement of the physical change including fringe (lamellae) length, tortuosity (curvature), and stacking. The chemical change is measured with EELS in TEM mode and taken from entire primary particles. TEM micrographs of the particles after heating with 1-4 pulses are displayed in Figure 6-12. A progressive structural order increase is seen, leading to well-defined concentric shells after heating with four pulses. The percentage of fringes greater than 3 nm is plotted in Figure 6-13. The nascent carbon black is comprised mainly of fringes less than 3 nm and after the first pulse the majority of fringes are longer than 3 nm. The bonding and hence growth of neighboring lamellae occurs rapidly. Subsequent pulses do not result in an increase in fringes greater than 3 nm. This is likely due to a limit in contrast resolution, due to fringes extending out of the focal plane and thus a technique limitation and not a true physical plateau.



Figure 6-12. R250 heated with 50 mJ/cm<sup>2</sup>: one pulse (A), two pulses (B), three pulses (C), and four pulses (D).



Figure 6-13. %-Fringes greater than 3nm from R250 - 50 mJ/cm<sup>2</sup> 1-4 pulses.

Lamellae growth in two dimensions is followed by restructuring in the third and measured by the stacking code, as shown in Figure 6-14. As seen the nascent carbon black is composed mainly of unstacked lamellae. Where a stack is defined by a maximum layer spacing, mid-point to mid-point distance and angle as was described in Section 3.4.4. With increasing number of pulses the stacking distribution shifts to more lamellae per stack. The well-known structural transformation based on HTT shown in Figure 2-25 states that the final stage of annealing following growth and reorientation is the de-wrinkling of the layer planes. This de-wrinkling is quantified by a decrease in fringe tortuosity and plotted in Figure 6-15. Tortuosity progressively decreases with increasing pulse number. Lamellae growth (fringe length), reorientation (stacking) and de-wrinkling (tortuosity) are all measures of physical changes occurring during the annealing process. The accompanying chemical change is the conversion of sp<sup>3</sup> hybridized carbon to sp<sup>2</sup> hybridized carbon. The initial sp<sup>2</sup> character found in the nascent carbon black is ~ 90 %. Upon the first pulse the sp<sup>2</sup> character increases to 100 % ( $\pm$  3). Additional pulses do not convert any fraction of the material back to sp<sup>3</sup> character at this laser fluence and pulse number range.



Figure 6-14. Stack distributions from R250 - 50 mJ/cm<sup>2</sup> 1-4 pulses.



Figure 6-15. Tortuosity distributions from R250 - 50 mJ/cm<sup>2</sup> 1-4 pulses.

All of the metrics quantified here show increasing order with additional pulse number. Therefore, it appears the material will complete the annealing transformation and reach the structure found from furnace heating with additional pulses. However, some ablated material is observable on the particle perimeter after heating with three pulses and is shown between particles after four pulses. Therefore, annealing and ablation are competing, with annealing more observable for pulse numbers 1-4. With an increase in pulse number to 10 and 100 annealing gives way to ablation. The structure after 10 pulses is shown in Figure 6-16.



Figure 6-16. R250 - 10 pulses 50 mJ/cm<sup>2</sup>.

As shown the order found after four pulses is destroyed by ablation when heated with 10 pulses. It seems counter institutive that the more ordered structure found after four pulses becomes more susceptible to ablation. The observed initial annealing and apparent lack of ablation is due to the greater mobility of short lamellae. The short lamellae are able to move about and rearrange during periods of elevated temperature. After four pulses, the lamellae are constrained and are unable to accommodate the energy addition via rearrangement. At elevated temperature the lamellae attempt to straighten out and the underlying layers exert a force on the outer layers. The outer layers partially detach leading to the chaotic disordered structures.

This further exemplifies that the material transformation trajectory is altered verses traditional furnace heating by Nd:YAG laser heating. The structure found after a 100 pulses is shown in Figure 6-17. The structure bears no resemblance to the starting material.



Figure 6-17. R250 - 100 pulses 50 mJ/cm<sup>2</sup>.

# 6.2 Nd:YAG Laser and Furnace Annealing of Sulfur Doped Synthetic Soot

As discussed and demonstrated in Section 4.4 the heteroatom sulfur effects carbon structure in a different way as compared to oxygen. Sulfur is thermally stable in carbon up to ~ 1,000 °C and therefore plays little role in the initial low temperature (500 °C) carbonization. As such, sulfur imparts a relatively unobservable impact on nanostructure as observed from coke, but rather acts to cause micro-cracks upon rapid evolution in the form of H<sub>2</sub>S and CS<sub>2</sub> upon subsequent graphitization heat treatment. The micro-cracks result in an observed volume increase and therefore the process has been termed puffing.<sup>41,143,148</sup>

In this section laboratory generated synthetic soots with and without sulfur doping are used to assess the impact of sulfur evolution on carbon structure. The defect sites formed upon sulfur release and their effect on nanostructure are not readily apparent in bulk coke. Soot rearrangements are isolated by primary particles and thus changes are readily observable. The samples were produced in a tube furnace as described in Section 3.1.2 from benzene and a 1:1 blend of benzene and thiophene. The two nascent materials are visually equivalent as seen in the HRTEM micrographs in Figure 6-18. Initial hydrogen wt.% as measured with a CHN analyzer is 1.15 for both materials. The sulfur doping level was measured with EDS and shown in the EDS map in Figure 6-19B. As shown in the EDS map, the sulfur is uniformly dispersed throughout the material.



Figure 6-18. HRTEM micrographs of synthetic soot derived from benzene (A) and benzene/thiophene (B).



Figure 6-19. HAADF micrograph (A) and EDS map (B) of benzene/thiophene synthetic soot.

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The measured sulfur content is 7.6 wt.%. Accounting for the 1.15 wt.% hydrogen that is undetectable with EDS, the wt.% of sulfur is 7.5. This is an appreciable level of sulfur doping as coke with 2.5 wt.% sulfur puffed as shown in Section 4.4.

Both materials were annealed with a single Nd:YAG laser pulse of 50 mJ/cm<sup>2</sup> and in a furnace at 2,600 °C for a one hour duration. A laser fluence of 50 mJ/cm<sup>2</sup> was selected because as shown in the preceding section, a single pulse at this energy acts to anneal carbon black and not ablate or vaporize the material. The sulfur evolution during conventional furnace annealing occurs after the carbon partially anneals. Rapid laser heating results in simultaneous annealing and sulfur evolution. The structure of the pure benzene synthetic soot after traditional graphitization heat treatment is the closed shell polyhedral, similar to furnace annealed carbon black shown in Figure 6-1. Furnace annealing of the benzene-thiophene sample also results in similar polyhedral structure. However, some (~ 5%) or the primary particles suffered significant damage from the explosive evolution of sulfur species as shown in Figure 6-20.



Figure 6-20. TEM micrographs of furnace annealed benzene/thiophene synthetic soot.

The dashed arrow in A shows an exit point that self-healed and closed. This point may have acted as the sulfur exit point for a few of the neighboring particles and thus would explain why not all the particles show obvious damage. The solid arrow in A shows a region where the facets did not rejoin after bursting open under the high pressure induced by the rapid evolution of sulfur. The micrograph in B shows an exploded particle. The result is similar

to the micro-crack formation found in cokes. However, cracks are manifested in primary particles as the escaping gases must break free from already partially annealed primary particle in order to escape. The sulfur content of the furnace annealed sample was below the EDS detection limit. The sulfur displayed in the EDS map in Figure 6-21 is the background noise from Bremsstrahlung braking radiation. Once removed from the spectra, no sulfur peak was observed.



Figure 6-21. EDS map of furnace annealed benzene/thiophene synthetic soot.

As seen from traditional furnace (i.e. slow ramp rates) heating, the carbon is able to sufficiently anneal prior to the onslaught of sulfur evolution and thus explosive pressure builds up the carbon walls. With Nd:YAG laser annealing, the annealing and sulfur evolution occur at the same time. Therefore, the defect left behind after sulfur evolution impacts the unset carbon nanostructure. HRTEM micrographs of both benzene and benzene/thiophene synthetic soot after Nd:YAG laser heating are given in Figure 6-22. The straight benzene sample anneals in a similar fashion to that already observed from the commercial carbon black heated with 50 mJ/cm<sup>2</sup>. The transformation found after laser annealing the sulfur doped sample is drastically different. The material is comprised of highly curved structures. The extent of annealing is also less as observed by the disordered wavy lamellae along the perimeter. The sulfur content found in the laser heated sample was below detection limits and only background noise Bremsstrahlung radiation is falsely identified as sulfur as displayed in the EDS map in Figure 6-23. The EDS map is an HAADF micrograph that is also useful for assessing thickness, obvious void spaces between the carbon ribbons are seen as compared to the homogenous thickness in the nascent material (Figure 6-19A). The curvature found in the laser heated sulfur doped

sample is an effect of overlapping the early annealing steps with sulfur evolution. When sulfur is released a defect is left behind and this defect may lead to the formation of curvature inducing odd membered rings. By rapid heating the carbon material, sulfur has much the same effect that oxygen does during low temperature carbonization.



Figure 6-22. HRTEM micrographs on benzene (A) and benzene/thiophene (B) synthetic soot after Nd:YAG laser annealing with 50 mJ/cm<sup>2</sup>.



Figure 6-23. EDS map of laser annealed benzene/thiophene synthetic soot.

#### 6.3 CO<sub>2</sub> Laser Annealing

CO<sub>2</sub> laser annealing of carbon black results in a final structure identical to that obtained from traditional furnace annealing as was the case for cokes and chars. The TTHs from heating a powder bed of R250 are experimentally identical to CO<sub>2</sub> heating of coke and char, previously displayed in Figure 5-13. In this section, commercial carbon black (R250) is annealed with the CO<sub>2</sub> laser without the use of the beam expander. Commercial carbon black is formed under temperatures similar to the maximum temperature achieved with use of the beam expander ~ 1,700 °C. Thus, higher temperatures are required to induce noticeable changes in the material. The isothermal heating temperature is  $\sim 2,600$  °C. A thin layer (few hundred µm) of carbon black was smeared onto carbon planchets, heated, and then the top most layer was collected for TEM analysis. Due to the nature of carbon black (i.e. loose aggregates) temperature measurements from the underlying surface was not possible due to sample retention. The thin layer was not uniformly heated, as was evident by non-uniform annealing extents found upon TEM examination. Conductive heat transfer is limited by higher thermal resistance, owed to the many junctions in an assembly of nanoparticle contact points. The most annealed particles found from a given laser pulse duration are presented here.

Visual material transformations were first observable after annealing for 100 ms and displayed in Figure 6-24.



Figure 6-24 HRTEM micrographs of nascent carbon black (A) after 0.1 seconds of CO<sub>2</sub> laser annealing (B).

The lamellae shown in B after annealing for 100 ms are longer than the nascent carbon lamellae shown in A. The disorganized center is beginning to reorganize and grow. As the center material grows, it stretches out towards the exterior in an effort to straighten. HRTEM micrographs after annealing for one and five seconds are shown in Figure 6-25. The lamellae after one second are longer and straighter than after 100 ms. The increased void space in the center is from densification of the carbon material. The reported density of carbon black ranges between 1.0 and 1.6 g/cm<sup>3</sup>.<sup>151–153</sup> Where graphitic carbons are ~ 2.0-2.2 g/cm<sup>3</sup>. Therefore, the hollowing of the center is simply the annealing of amorphous to ordered carbon and becomes more pronounced as the stacks straighten. After five seconds the lamellae undulate less. However, the stacks themselves still have a wave-like structure. HRTEM micrographs after annealing for 10 and 20 seconds are provided in Figure 6-26. By 10 seconds the wave-like structure in the stacks is reduced and the joints found between the facets of the multifaceted polyhedron end structure are starting to take shape, as highlighted by the arrow in A. After annealing for 20 seconds the structure is equivalent to furnace annealing at 2,600 °C for a duration of one hour as shown by the multifaceted polyhedron in B.



Figure 6-25 HRTEM micrographs after 1 (A) and 5 (B) seconds of CO<sub>2</sub> laser annealing.



Figure 6-26 HRTEM micrographs after 10 (A) and 20 (B) seconds of CO<sub>2</sub> laser annealing.

## 6.4 Summary

As was the case for cokes and chars, Nd:YAG laser heating of carbon black results in ablation and vaporization. Whereas CO<sub>2</sub> laser heating is equivalent to traditional furnace annealing. Although the carbon blacks are initially more resilient to ablation from Nd:YAG laser annealing, they ultimately ablate upon increasing pulse number. Furnace annealing of sulfur doped synthetic soot results in cracks and rupturing due to the high pressures caused by explosive sulfur evolution at elevated temperature. Whereas Nd:YAG heating of the sulfur doped sample acted to induce curvature. The observed curvature is owed to annealing occurring simultaneously with sulfur evolution. The unset lamellae are strongly influenced by the defect formed upon sulfur evolution.

## **Chapter 7**

# Laser Processing of Carbon Material

In this chapter a few potential applications of laser carbon material processing are discussed. Applications presented here are those that cannot be performed by traditional furnace annealing. This is far from an exhaustive list and lasers are poised to be instrumental in the advancement of carbon science and technology.

#### 7.1 Continuous Annealing

Perhaps the most over looked application of laser annealing carbon is the ability to do so continuously and rapidly. Graphitization furnaces operate as a batch processing system. Time from start to completion is on the order of a day due to the slow (~25 °C/min) heating rates, long hold times, and slow cooling of the heavily insulated furnace. Additionally, these furnaces require routine maintenance and replacement of expensive graphite heating elements, bolts, posts, and specialty graphite fiber insulation. As demonstrated throughout this dissertation, CO<sub>2</sub> laser annealing provides equivalent material transformation on the order of seconds and modern CO<sub>2</sub> lasers are designed for years of maintenance free use. Although laser annealing is limited to thinner material due to limited heating depth, materials can be annealed continuously and with potentially high throughput. Higher power lasers and use of multiple lasers can likely uniformly anneal bulk materials as well. The CO<sub>2</sub> laser used in this dissertation is 250 W at maximum power and industrial CO<sub>2</sub> lasers have output powers of tens of kW. With the temporal control of lasers, the annealing extent can be controlled based on specific application focus. The power and therefore temperature can also be modified on demand.

### 7.2 Oxidative Surface Treatment

The majority of all manufactured carbon black is used as a reinforcing agent in rubber with automotive tires accounting for 70% of total carbon black demand.<sup>10</sup> The desired material properties that make carbon black a good reinforcing agent for rubber are high surface area and high mechanical integrity. The 8 ns Nd:YAG laser pulse can be used to simultaneously increase surface area via kinetically limited oxidation while increasing the overall particle integrity via annealing the interior. As shown in the TEM micrographs in Figure 7-1 the oxidation is kinetically limited to the outer surface and the interior is thus protected from oxidation and anneals. The carbon black was heated in open air.



Figure 7-1. TEM micrographs of Nd:YAG laser annealed carbon black in open air.

The treatment could be performed in situ during carbon black production by adding in optically transparent windows. Controlled surface modification via kinetically limited oxidation may potentially be useful for many other materials.

## 7.3 Selective Laser Sintering

During  $CO_2$  laser annealing of carbon black in an inert environment, connecting of the aggregates was observed to take place. The connections formed are shown in the HRTEM micrographs in Figure 7-2.



Figure 7-2. HRTEM micrographs of laser sintered carbon black.

The connections shown in Figure 7-2 have ordered structure and thus are unlikely a result of solidified carbon vapor. The connection is likely a result of a perimeter carbon stack or singular layer partially detaching from the particle and connecting to the neighbor. This type of connection was common when annealing with high energy 100  $\mu$ s CO<sub>2</sub> laser pulses (i.e. 16.36 J/cm<sup>2</sup>). The connections are highlighted in the TEM micrograph in Figure 7-3.



Figure 7-3. TEM micrograph of laser sintered carbon black.

The product material is assumed to have increased electrical conductivity based on the observed structure. The connections may provide long range electrical conductivity as compared to starting carbon black. These connections were made without additional material. Laser sintering a mixture of materials could result in a wide range of potential applications.

# 7.4 Thin Films

Carbon films serve in a wide range of applications from space craft heat shielding<sup>154,155</sup> to semiconductor masks<sup>156</sup>. Annealing of such films is limited by the underlying substrate (i.e. carbon annealing temperatures exceed substrate melting point). In the case of carbon hard masks that protect semiconductors during plasma etching, the carbon deposition and any post annealing must be under 600 °C as not to damage the underlying silicon.<sup>157</sup> The amorphous carbon films can have high hydrogen content >20 atomic %.<sup>158</sup> Annealing of the amorphous film would make for a more protective mask. However, 600 °C is not high enough to anneal the film in a meaningful way and thus furnace annealing cannot be used. Lasers can be used to anneal just the carbon film and not damage the underlying substrate.

As a demonstration, a pyrolytic carbon formed from CVD of ethylene deposited on a Cu substrate was annealed with the CO<sub>2</sub> laser. Details about this material have been previously provided in an unrelated study.<sup>159</sup> An SEM micrograph of the film and underlying substrate are shown in Figure 7-4.



Figure 7-4. SEM micrograph of pyrolytic carbon film.
The carbon film is between 200-400 nm thick. After laser annealing directly from the top, no apparent changes to the film morphology or underlying Cu substrate were observed in the SEM. The top surface was annealed with 1000 one ms long laser pulses. The pulses were delayed from one another by 50 ms to provide adequate cooling between pulses. The total processing time is less than one minute. Sections of the film were removed from the substrate and crushed in a mortar and pestle both before and after laser annealing for TEM analysis. The films nanostructure before and after annealing are displayed in the HRTEM micrographs in Figure 7-5.



Figure 7-5. HRTEM micrographs of virgin pyrolytic carbon (A) and laser annealed (B).

As seen in Figure 7-5, laser annealing resulted in a significant improvement in material order. The more crystalline laser annealed material will be more resilient and make for an improved carbon hard mask. Laser annealing did not damage the underlying substrate. As carbon film applications continue to increase so will the potential utility of laser annealing.

#### 7.5 Porous (Swiss-Cheese-Graphite) Graphite

In Section 4.3.2 anthracene and fluorene were co-carbonized and it was observed that the optical texture present in the coke product was partially destroyed upon furnace graphitization heat treatment. The structure as observed in the TEM was heterogeneous and comprised of both graphitic and highly disordered regions, see Figure 4-25. The graphitic regions are from annealed anthracene coke. The structure found in the disordered regions is the same as that found after heat treatment of pure fluorene char. The disordered regions were likely present in the virgin coke as fluorene derived pitch. Since the disordered regions are below the detection size limit in a light microscope, the pitch was not resolved in the polarized light micrograph from the virgin coke, Figure 4-23. Upon heat treatment at 2,600 °C for 1 hour the pitch forms the disordered carbon regions causing stress between adjacent graphitic regions that results in misalignment between the graphitic regions. This misalignment translates to a decreased optical texture size as observed in the polarized light micrographs from before and after heat treatment.

 $CO_2$  laser annealing vaporizes out the fluorene derived pitch and graphitizes the anthracene coke. The resulting structure is that of graphite with ~ 200 nm spherical pores as shown in Figure 7-6. The Swiss cheese like structure in Figure 7-6 was prepared by  $CO_2$  laser annealing at 2,600 °C for a duration of one minute. Traditional annealing of this material does not result in the porous structure as the heating rates are far too slow to vaporize out the pitch.



Figure 7-6. TEM micrographs of Swiss-Cheese-Graphite formed from CO<sub>2</sub> laser annealing of anthracene/fluorene coke.

The vaporization of the fluorene pitch is rapid and Swiss-Cheese-Graphite is produced with very short laser pulses. Longer laser pulse widths are utilized to anneal the remaining anthracene coke. A thin carbon film from the deposition of the vaporized fluorene pitch was found around the annealed sample. A TEM grid was placed near the sample for the purpose of collecting the film. A TEM micrograph of the deposited carbon product is shown in Figure 7-7. As seen in the micrograph the film is in the form of soot and thus supports the assumption of vaporized pitch leaving behind the pores as the pyrolysis of pitch in aerosol will result in the formation of soot.



Figure 7-7. Soot formed from CO<sub>2</sub> laser vaporization of fluorene carbonization pitch.

Swiss-Cheese-Graphite after one minute of  $CO_2$  laser annealing has a d<sub>002</sub> spacing of 3.40 Å, the same as pure anthracene coke and thus the pores do not limit graphitizability. The laser synthesized Swiss-Cheese-Graphite was heat treated at 2,600 °C for a one hour duration in a graphitization furnace. The layer plane spacing measured with XRD is 3.36 Å, the same as pure anthracene coke.

A potential application of porous Swiss-Cheese-Graphite is as the lithiated anode for lithium ion hybrid battery-supercapacitors. Most of the capacitor research effort is focused on the cathode and activated carbons with extremely high surface areas are used.<sup>160,161</sup> A hybrid battery-capacitor combines the properties of the two devices. Lithium ion batteries have high energy density, but suffer from low power by virtue of reversible Coulombic reactions that occur at both electrodes.<sup>162</sup> The high energy density of the lithium ion battery is owed to the intercalation of lithium in the graphite anode material. On the end of the spectrum, electrochemical double-layer supercapacitors store energy by accumulation of ions on the surface of high surface area electrode materials. The supercapacitor has high power density, but low energy storage capacity. Efforts to combine the high energy density of the battery and high power density of the supercapacitors total stored charge is proportional to the amount of each component, the power and energy performance is decoupled.<sup>162,163</sup> A success hybrid must not simply be configured from current components from the two devices, but from a hybrid electrode.

Graphite is the most common anode material for lithium ion batteries. However, the rate capacity of charging and discharging the lithiated graphite anode is a limiting factor for hybrid battery-capacitors. The porous Swiss-Chees-Graphite may provide improved rate capacity as the pores will increase lithium intercalation and deintercalation rates while retaining the desired properties of graphite (i.e. high energy density). The ideal porous graphite should contain small pores covering the entire material and the graphite pore interface needs to be accessible to Li.

As seen in the TEM micrograph in the right side of Figure 7-6, not all of the laser annealed anthracene-fluorene coke contains pores. The pore dispersion illustrated in the left micrograph of Figure 7-6 was present in approximately 1/4 of the material observed. Such low pore dispersion is undesired for the anode material used in hybrid battery-capacitors. Worse yet, is the pore wall structure as shown in the TEM micrograph in Figure 7-8. The pore walls are comprised of closed shell nanoparticles and thus the graphitic layers are inaccessible to Li ions.



Figure 7-8. TEM micrograph of pore wall from anthracene-fluorene derived porous graphite.

To optimize Swiss-Cheese-Graphite the five membered ring containing fluorene compound was replaced with pyrene as the fullerenic-like structures around the pore walls may likely be due to the odd membered ring. It has been repeatedly observed that oils with higher concentrations of pyrene results in extended fluidly of the carbonization medium.<sup>41,55,56</sup> Pyrene functions as a hydrogen shuttler and good solvent, extending fluidity and moderating the reactivity of the carbonizing medium. Co-carbonization of pyrene and anthracene yielded mostly tar after five hours at 500 °C. However, the solid product did yield Swiss-Cheese-Graphite upon laser annealing and the pore walls were unimpeded by fullerenic structures. To increase the yield an equal part blend of anthracene-pyrene-fluorene was carbonized. The solid carbon yield was 40 wt.% after carbonization at 500 °C for five hours. The laser annealed product is shown in the TEM micrograph in Figure 7-9. As seen in Figure 7-9B the graphitic layer planes are unimpeded.



Figure 7-9. TEM micrographs of Swiss-Cheese-Graphite.

Vertical agitation of the reactors was increased to a frequency of 300 oscillations a minutes during the isothermal heat treatment. This recipe yields small pores of ~ 100 nm covering more than half of the material and the graphitic pore interface is accessible to Li. Therefore, this material is a promising candidate for the lithiated anode in hybrid battery-capacitors. The material is currently being tested in a test cell. A slurry of Swiss-Cheese-Graphite was coated on copper foil to make ~ 50 micron thick electrodes and was lithiated using a short circuiting approach to make a half cell.<sup>164</sup> The cell is being used to systematically study the capacity of the electrode at different current densities (0.1 - 10 A/g).<sup>164</sup>

## **Chapter 8**

## **Conclusions and Recommendations for Future Work**

#### **8.1 Conclusions**

This study focused on laser-carbon interactions with emphasis placed on annealing. The research encompassed identifying heating rates and time at temperature that resulted in annealing following the traditional furnace pathway. With use of the high temporal control provided via laser annealing, the extent and trajectory of annealing was followed during the early annealing stages. Anthracene coke and sucrose char were selected as the model graphitizable and non-graphitizable carbons based on historical precedence. Furnace annealing of cokes and chars produced from: oxygen containing compounds (polyfurfurly alcohol and anthanthrone), from the five membered ring containing PAH (fluorene) and a blend of anthracene-fluorene, and from sulfur containing decant oil and a blend of anthracene coke and sucrose char. A commercial carbon black (R250) and laboratory generated synthetic soot from benzene and benzene-thiophene were laser and furnace annealed.

Material transformations were measured with HRTEM, EDS, SAED, and EELS. Virgin samples and traditional furnace annealed samples available in bulk were analyzed with XRD as well. Laser annealed materials were compared to furnace annealed samples held at matching temperatures for one hour.

The main findings are:

- 1. The nanostructure of non-graphitizable chars produced from oxygen containing precursors are identical to chars embedded with odd membered carbon rings.
- 2. The non-graphitizability of chars formed from oxygen rich precursors is due to the formation of odd membered carbon rings upon oxygen evolution during low temperature carbonization.
- 3. The energy dense Q-switched Nd:YAG laser heats carbon above graphitization heat treatment temperature within nanoseconds. The material transformation trajectory is altered verses traditional furnace heating at these rapid heating rates ≥ 3.5 x 10<sup>11</sup> °C/s and short times above temperature (above 2,000 °C for 1.5 µs).
- 4. A continuous wave CO<sub>2</sub> laser heats carbon samples to graphitization heat treatment temperature with a ramp rate of ~ 1,840,000 °C/s and brings the sample to 2,600 °C in 1.4 ms. At this heating rate and time at temperature, samples follow the traditional furnace annealing pathways as based upon the equivalent end structures obtained from matching temperatures.

- 5. Pulsing the CO<sub>2</sub> laser with a pulse generator allowed for the trajectories with respect to time at temperature to be followed.
- 6. Sucrose char passes through a structural state of completely closed shell nanoparticles that open upon additional heat treatment and give rise to the irregular pore structure found in the end product. The observed curvature in sucrose char annealed at 2,600 °C is a result of shell opening and thus odd membered rings are not manufactured during the annealing process due to impinging growth of stacks, they are present in the starting structure.
- 7. Furnace annealing of sulfur doped synthetic carbon resulted in cracks and rupturing due to the high pressures caused by explosive sulfur evolution at elevated temperature. The effect is similar to micro-crack formation caused by puffing in sulfur rich cokes. Nd:YAG laser heating of the sulfur doped synthetic soot acted to induce curvature in the nanostructure due to annealing and defect formation from sulfur evolution occurring simultaneously.
- 8. Laser annealing carbon is potentially of enormous technological importance as annealing can be performed continuously and rapidly. Additionally, material processing and synthesis not possible via traditional annealing can be used in the development of novel materials.

#### 8.2 Recommendations for Future Work

Non-graphitizable chars produced from oxygen rich precursors like PFA and char from fluorene should be annealed with the  $CO_2$  laser for the purpose of following the trajectories with respect to time above temperature. The final end structures of furnace annealed PFA char, fluorene char, and sucrose char are equivalent. It is likely that PFA char and fluorene char both pass through a structural state of completely closed shell nanoparticles that open upon additional heat treatment and give rise to the irregular pore structure found in the end product. This mechanism may well account for the end structure in many non-graphitizable carbons and should be further tested.

Selective laser sintering of a mixture of materials may result in structures of high value. One such desired outcome would be the controlled attachment of single walled CNTs to a host material such as carbon black.

The porous (Swiss-Cheese-Graphite) graphite that is currently being tested as an anode material for hybrid battery-capacitors can be further optimized. Smaller pores with higher dispersion are desired. Increased reactor agitation may aid is pore dispersion and should be explored. Different heat treatment schemes can likely speed up the production time (i.e. higher temperature and shorter soak time). Mild activation will likely open additional pores that closed off during laser annealing as assessed by the low surface area of the material (~  $30 \text{ m}^2/\text{g}$ ). However, the pores are still likely accessible to lithium as lithium is much smaller

than the nitrogen used in surface area measurements. The current recipe calls for high purity model compounds. For the purpose of cost reduction cheaper feedstocks should be explored. As a first step anthracene can be replaced with cheap readily available decant oil as the graphite precursor. Identifying a cheap tar precursor that disperses homogenously throughout the material and is vaporized out upon laser heating will be more challenging.

Comparative ReaxFF atomistic simulations would provide a great compliment to the observed experimental findings and advance the underlying material science.

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# Appendix

### Nd:YAG laser heating of anthracene coke after furnace annealing at 1,200 °C for 1 hour

As demonstrated in Section 5.1, even at low laser fluences, material ablation occurs from heating with energy dense Q-switched laser pulses. Carbon black was shown to be more resistant to ablation in Section 6.1. Carbon blacks are formed under higher temperatures than cokes and chars and thus have higher carbon to hydrogen ratios. To test if ablation is solely due to starting structure (i.e. crystallinity and chemistry) or if it is the primary outcome of Nd:YAG laser heating, anthracene coke annealed at 1,200 °C for a duration of 1 hour was heated with the Nd:YAG laser. The commercial carbon black used in Section 6.1 has a hydrogen wt. % of 0.25 as compared to virgin anthracene coke at 4.0 wt. %. The hydrogen wt. % of anthracene coke after annealing at 1,200 °C for a 1 hour duration is 0.19.

The structure as observed by TEM after heating with a single laser pulse of 100 mJ/cm<sup>2</sup> is shown in Figure A-1.



Figure A-1. TEM micrograph of anthracene coke annealed at 1,200 °C for 1 hour and subsequently laser heated with 100 mJ/cm<sup>2</sup> Nd:YAG laser pulse.

As compared to virgin anthracene coke heated with the same laser fluence (Figure 5-5 A and B), the material is more annealed and less ablated. However, the transformation still resembles ablation as illustrated by the expansion at the edge of the structure in Figure A-1A. The structure is very similar to that found from Nd:YAG laser heating of carbon black in Section 6.1. The carbon black and the anthracene coke heated here have very similar starting hydrogen contents. Therefore, the staring structure and initial chemistry (i.e. hydrogen and heteroatoms) controls the initial ablation resistance. Higher hydrogen

content may result in increased ablation due to rapid devolatilization upon Nd:YAG laser heating. Although carbon black was more resilient to ablation as compared to virgin anthracene coke, it ablated nonetheless with addition pulses. The structure of anthracene coke annealed at 1,200 °C for 1 hour and subsequently heated with 10 Nd:YAG laser pulses of 50 mJ/cm<sup>2</sup> is shown in Figure A-2.



Figure A-2. TEM micrograph of anthracene coke annealed at 1,200 °C for 1 hour and subsequently laser heated with 10 pulses of 50 mJ/cm<sup>2</sup>.

As seen in Figure A-2, even with a low laser fluence (50 mJ/cm<sup>2</sup>) heating with multiple pulses acts to destroy the material via ablation. The remnants of what were the graphitic like bands can yet be made out in Figure A-2. The layers are stripped away with additional pulses, leaving behind the expanded and disorder material. Closed shell fullerenic structures are present. Therefore, Nd:YAG laser heating is equivalent to ablation regardless of staring carbon structure. However, more pure carbons (i.e. low hydrogen and heteroatoms) are initially more resistant to ablations.

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